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Ion-activity products of some apatite minerals

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Ion-activity products of some apatite minerals

by

Sen-Hsiung Chien

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TABLE OF CONTENTS

INTRODUCTION

Minerals of the apatite group occur in dispersed form in rocks and soils and in concentrated form in phosphate rock and the hard tissues (teeth and bones) of animals. Apatites are used to some extent for direct application to soils as a source of phosphorus for plants. In contrast to superphosphate and other soluble phosphate fertilizers, the availability of which rapidly decreases due to chemical reactions with soils, the apatite minerals have relatively low solubility, and they react only slowly with soils. The problem with the apatites is that they may not provide enough phosphorus in solution to make them effective as fertilizers. Their solubility is thus of great importance.

The solubility of apatites has been investigated extensively. Most of the research has dealt with hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, and fluorapatite, $Ca_{10}(PO_4)_6F_2$, principally the former. The interest in hydroxyapatite is related to the occurrence of this substance in the hard tissues of animals. There has been considerable controversy with regard to the solubility relations of hydroxyapatite. Some investigators consider that hydroxyapatite does not possess a solubility-product constant. Others consider that the solubility of hydroxyapatite is controlled by a "surface complex" that has a chemical composition different from that of hydroxyapatite. Others consider that a certain solubility-product constant, but those who do so have not agreed on what the value of the constant may be.

Little work has been done on the solubility-product constant of the apatite in phosphate rocks, one reason being that the chemical nature of

the apatite was not clear. Recent work indicates that the composition of the apatites of phosphate rocks may differ considerably from one rock to the next but that nearly all the sedimentary phosphate rocks, which supply the great bulk of the phosphorus used for chemical processing and for direct application without processing other than fine grinding, are carbonate apatites, known also as francolites or substituted fluorapatites in which CO_3 + F replace some PO_4 and Na + Mg replace some Ca.

The objectives of the work reported in this thesis were to obtain information on the following questions: (1) Does hydroxyapatite have a solubility-product constant? (2) Do the carbonate apatites in phosphate rocks have a solubility-product constant? (3) Is there a relationship between the degree of carbonate substitution in the carbonate apatites of phosphate rocks and the solubility of the apatites? It was considered that the information obtained in these investigations should contribute to an understanding of the dissolution of phosphate rocks in soils and to the potential value of different phosphate rocks as fertilizers in different soils.

REVIEW OF LITERATURE

Nature of Hydroxyapatite

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, occurs naturally (Palache et al., 1951) and is the stable end-product when more soluble calcium phosphates are treated with water to remove dissolved constituents (Schleede et al., 1932) in the absence of fluoride. An apatite, not necessarily hydroxyapatite, has been identified in the so-called water-insoluble fraction of phosphate fertilizers (Ando et al., 1965; Brosheer and Lenfesty, 1958; Terman et al., 1962), in soils treated with phosphate fertilizers (Lehr and Brown, 1958; Nagelschmidt and Nixon, 1944), and in crystalline products formed in phosphate solutions that had been in contact with soil (Beaton et al., 1963; Larsen and Widdowson, 1966; Lindsay et al., 1962).

Hydroxyapatite has been considered the major constituent of all hard tissues of animals since the early X-ray diffraction investigations by Dejong (1926). In biological materials, hydroxyapatite is invariably very finely subdivided, with a high specific surface (Avnimelech et al., 1970).

According to Posner (1960), the crystal form of hydroxyapatite falls in the dipyramidal space group (i.e., symmetry group) of the hexagonal class, with unit-cell dimensions of $\underline{a}$ = 9.432 Å and $\underline{c}$ = 6.881 Å. The formula, $Ca_{10}(PO_4)_6(OH)_2$ represents the unit-cell contents, that is, the fundamental chemical repeating unit in the three-dimensional symmetry pattern of the crystal. Lehr et al. (1967) reported the lattice constants of hydroxyapatite as $\underline{a}$ = 9.415 Å and $\underline{c}$ = 6.878 Å. Young and Elliot (1966) described the arrangement of atoms in a unit cell. Lehr et al. (1967)

published data on optical properties, X-ray diffraction pattern, infrared absorption spectrum, and other properties of hydroxyapatite.

A procedure to prepare pure, well crystallized hydroxyapatite was proposed by Perloff and Posner (1960). The procedure involves preparing pure $CaHPO_4$ and hydrolyzing it to hydroxyapatite in a hydrothermal bomb at 300° C. They suggested that one or both of the following reactions may be involved in the hydrolysis:

$$10\ CaHPO_4 + 2\ H_2O = Ca_{10}(PO_4)_6(OH)_2 + 4\ H^+ + 4\ H_2PO_4^-$$

$$14\ CaHPO_4 + 2\ H_2O = Ca_{10}(PO_4)_6(OH)_2 + 4\ Ca^{++} + 8\ H_2PO_4^-$$

Perloff and Posner reported that their bomb method produced well-developed, clear, hexagonal, dipyramidal crystals of hydroxyapatite up to 0.3 mm in length.

Recently, Avnimelech et al. (1970) prepared a pure, finely divided hydroxyapatite by titrating a calcium hydroxide slurry at boiling temperature with phosphoric acid. A high pH, a high temperature, and slow addition of reagents were used to limit the formation of metastable calcium phosphates. The preparation was then boiled for several days to improve the crystallization. The specific surface of the product was reported to be 26 m^2 per gram.

The X-ray diffraction pattern of hydroxyapatite is exhibited by certain finely-divided calcium phosphates that do not have the theoretical ratio of calcium to phosphorus (Neuman and Neuman, 1953; Hendricks and Hill, 1950). There are two conflicting explanations for a low ratio of calcium to phosphorus in these hydroxyapatites. One is that an excess of phosphate is adsorbed on the surface of the tiny crystals of stoichio-

metric hydroxyapatite (Hendricks and Hill, 1950). The other is that there is some sort of statistical absence of calcium ions from structural positions throughout the crystal, with provisions for maintaining electrical neutrality (Posner et al., 1954). As the general formula for members of the apatite family, Posner (1960) suggested

$$D_{10-x}M_{2x}(PO_4)_6(OH)_2,$$

where D represents the divalent cation (Ca^{++}, Mg^{++}, Sr^{++}, Pb^{++}, etc.), and M represents the monovalent cation (Na^{+}, H^{+}, etc.).

Nature of Fluorapatite

Fluorapatite, $Ca_{10}(PO_4)_6F_2$, is another common member of the apatite family. Minute crystals of fluorapatite are found in small quantities in most igneous rocks. Sometimes fluorapatite is found in massive deposits (Kola Peninsula), in association with hematite deposits in hydrothermal veins, in metamorphic rocks, and in sedimentary deposits of marine origin (Palache et al., 1951). Fluorapatite may form in soils from reversion of less basic calcium phosphates in the presence of fluoride (Lehr et al., 1967). Murrmann and Peech (1968) found that the extracts of many limed soils were unsaturated with respect to hydroxyapatite but were saturated with fluorapatite in the presence of 10^{-5} molar fluoride solution (which was the concentration of fluoride in several of the extracts examined). Thus they concluded that fluorapatite was the ultimate reaction product of super-phosphate applied to the limed soils they investigated.

The structure of fluorapatite is similar to that of hydroxyapatite because the fluoride ion has the same ionic charge and almost the same size as the hydroxyl ion. Beevers and McIntyre (1946) reported that the

unit cell of apatite has two equal edges inclined at 120° to one another, with an a dimension of 9.37 Å in fluorapatite and 9.41 Å in hydroxyapatite. The third edge is at a right angle to the two equal edges and has the length c = 6.88 Å in both structures.

Wallaeys (1952) demonstrated isomorphous substitution in fluorapatite. He heated anhydrous tricalcium phosphate with mixtures of calcium fluoride and calcium chloride in the absence of water vapor at 800° C and found that the X-ray diffraction pattern obtained with the resulting solids showed a progressive transition from the pattern of fluorapatite to that of chlorapatite as more and more of the calcium fluoride in the original reaction mixture was replaced by calcium chloride. He interpreted his observations as a substitution of chloride ions for fluoride ions in the crystalline structure of apatite.

Substitution of carbonate ions for fluoride ions was reported by Chakravorty and Ghosh (1966). McClellan and Lehr (1969) disagreed with this idea and proposed that carbonate and fluoride ions together substitute in part for phosphate and that sodium and magnesium substitute in part for calcium. McClellan and Lehr's views will be discussed later in more detail.

Origin of Phosphate Rock

Vast deposits of phosphate rock occur at various places in the world. Most phosphate rocks would be classed as sedimentary rocks of comparatively recent geologic origin, but some are igneous and had their origin in the primeval molten magma. The name, "phosphorite," has been applied to the sedimentary deposits (Waggaman, 1952; Sauchelli, 1965). Apatite is the principal form of phosphorus in phosphate rocks -- carbo-

nate apatite in the sedimentary rocks and fluorapatite in the igneous rocks. The apatite in the sedimentary rocks is usually poorly crystallized (Smith and Lehr, 1966), and that in igneous rocks is well crystallized.

Various theories have been proposed for the origin of the sedimentary phosphate rocks known as phosphorite (Richardson, 1968). These theories may be separated into two groups, the physiocochemical theories and the biolith theories.

According to Kazakov's (1937) physicochemical theory, the chief source of phosphorus, calcium, and carbon is the mineralization of dead animal and plant tissue and the bottom sediments of deep ocean basins. As ocean currents move the cold water from great depths toward the surface and spread it over the continental shelves or platforms, the temperature rises, the partial pressure of carbon dioxide decreases, and part of the phosphorus is precipitated as phosphorite pellets on the shelves at depths of 50 to 200 meters.

McKelvey et al. (1953) and McKelvey (1959) modified this theory to state the possibility that deeper waters (400 to 1,000 meters) are the site of accumulation of the phosphorite. They also state that a pH slightly below 7.8 is also needed so the solubility-product of calcite will not be reached. As the pH rises in proceeding from the more acidic ocean depths to the more basic near-shore continental shelf area, the waters approach and then exceed saturation with fluorapatite and then with calcium carbonate. In contrast to Kazakov, they consider that organisms and their fecal pellets play a part in the precipitation of the compounds from solution by forming a nucleus upon which the

precipitate can build. Moreover, they note that the phosphorus and carbon dioxide being upwelled allow development of extensive blooms of plankton and nekton, which may contribute to the carbonaceous material in the phosphate deposits.

Pervear (1967) used the results of Ames' (1959) controlled laboratory experiments as a basis for a different kind of physicochemical theory. According to Pervear's theory, the mechanism that forms most phosphorites is chemical replacement of calcium carbonate by calcium phosphate when the former substance is bathed in a dilute solution of phosphate. Ames found that a solution containing as little as 0.1 ppm. of PO_4 would replace some calcium carbonate with calcium phosphate. Pervear stated that this concentration is reached only in estuaries, fiords, and upwelling environments.

According to the biolith theories, most phosphorite beds are formed by the accumulation of animal remains or of animal precipitates. Branson (1933) suggested that the calcium phosphate in phosphorite deposits might result from the accumulation of large quantities of cartilage and teeth of sharks and bones of other fish through a long period of time or during a period of mass destruction caused by a catastrophic physical change. The accumulation of conodants of brachiopod shells over a long period of time was suggested as another possibility.

Blackwelder (1915) suggested that the environment best suited to the accumulation of phosphate is the same as that for accumulation of black shale deposits. He considered that the ammoniacal solution caused by destruction of protein of dead animals by anaerobic bacteria was very important in formation of phosphorite because of the combination of a

high pH and reducing conditions that prevented the dissolution of the phosphate. Oxidizing conditions, he believed, would dissolve the phosphate.

McConnell (1965) suggested a theory similar to that of Blackwelder. He modified the theory by proposing that the phosphate is fixed by the bacteria or enzymes associated with dead animals. McConnell used as the basis for his theory the work of Ennever (1963), who found that bacteria and enzymes can concentrate phosphate ions from dilute solution.

Youssef (1965) suggested a biochemical mode of formation that is dependent on the configuration of the ocean floor. He observed that accumulations of phosphate are located in small basins on the continental shelf or slope which are crossed by strong ocean currents. Because of the strong moving currents, no precipitation occurs. In the basins, where there is a concentration of dead organisms, however, the bacteria fix the phosphate in biochemical precipitates. According to laboratory experiments, the pH of the water must be at or above 7.8 for this process to occur.

Nature of Apatite in Phosphate Rock

The apatite family includes a number of mineral species, of which hydroxyapatite and fluorapatite are the best known and most widely investigated. It is now well known that numerous isomorphous substitutions may occur in apatites and that the apatite in sedimentary phosphate rock contains carbonate. There has been disagreement, however, with regard to the mode of occurrence of the carbonate.

Chakravorty and Ghosh (1966) investigated phosphate rocks with infra-

red spectroscopy and considered that formation of carbonate apatite occurred by the replacement of fluoride or hydroxyl ions by carbonate ions and that the four phosphate rocks they examined were fluorapatite with partial substitution of fluoride by carbonate to form carbonate apatite. According to McClellan and Lehr (1969), this concept is incompatible with the structure of apatite as determined from X-ray diffraction investigations.

Another concept has been developed in connection with investigations of the state of carbonate in bone mineral. Neuman and Neuman (1953) suggested that carbonate and perhaps bicarbonate ions are sorbed on the surface of apatite crystals by exchange with phosphate. Thus, when a finely crystalline synthetic hydroxyapatite is equilibrated with a carbonate solution, it is found that the quantity of CO_2 taken up by the apatite is proportional to the ratio of carbonate to phosphate in the solution (Sobel et al., 1949). Posner and Duyckaerts (1954) demonstrated that the carbon dioxide can be almost completely removed from carbonate-bearing apatites by acid leaching without affecting the X-ray pattern.

A different concept of the occurrence of carbonate was developed by McConnell and Gruner (1940) and McConnell (1952). According to these investigators, carbonate ions substitute for phosphate in the apatite structure, with the consequence that the resulting apatite should be recognized as a true mineral species, to which the name, francolite, may be given. McConnell pointed out that francolite has a lower index of refraction and a greater optical birefringence than does fluorapatite, characteristics he interpreted as being consistent with the view that the carbonate substitutes for phosphate.

The McConnell theory was developed further by Borneman-Starinkevich and Belov (1953), who suggested that, when a planar carbonate ion substitutes for a tetrahedral phosphate ion, the vacant oxygen position is occupied by a fluoride ion. This carbonate-fluoride arrangement would have no mutual bonding, but it would preserve electrical neutrality in the structure and would complete the coordination of the cations. Elliott (1964) and McClellan and Lehr (1969) both accepted the Borneman-Starinkevich and Belov modification of the McConnell theory as the most reasonable concept available.

McClellan and Lehr (1969) studied the mineralogy and composition of the apatite fractions of 110 phosphate ores that represented nearly all the economically important deposits in the world. They adopted the theory described in the preceding paragraph and, with its aid, were able to develop further the understanding of the nature of the apatites in phosphate rocks. They found that the chemical composition and crystallographic properties of the apatite fraction of the phosphate rocks were well correlated. As the degree of substitution of carbonate for phosphate increased, the length of the crystallographic axes changed, and it was possible to estimate one from the other. Their chemical data indicated that only part of the carbonate that substituted for phosphate was accompanied by fluoride, and that the electrical unbalance thus created was corrected by substitution of some sodium for calcium. On the assumptions that the basic substitution is one carbonate for one phosphate and that electrical neutrality must be maintained, they represented the general formula for the apatite in sedimentary phosphate rocks as follows:

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{2+0.4x}$$

Solubility-Product Investigations

The solubility-product of apatite minerals has been under investigation for many years. Most of the work has been done in connection with studies of teeth and bones. Relatively little work has been done on the solubility-product of apatites in phosphate rocks. The solubility-product of compositions exhibiting the hydroxyapatite X-ray diffraction pattern has been the subject of a large amount of study because this information is thought to be needed for the proper understanding of the physiology of bone growth and the equilibrium of bones with body fluids.

Some investigators (Levinskas and Neuman, 1955; Neuman and Neuman, 1958) have suggested that hydroxyapatite exhibits incongruent solubility or does not have a true solubility-product constant because they found that the ratio of calcium to phosphorus in solutions equilibrated with hydroxyapatite varied with the ratio of solid to solution and, in general, was higher than that of the solid phase.

On the other hand, Clark (1955) presented data in support of the view that hydroxyapatite has a solubility-product constant and that its value is $10^{-115.5}$ (or that $pK = 10\ pCa + 2\ pOH + 6\ pPO_4 = 115.5$). Moreover, he found that solutions equilibrated with hydroxyapatite that had been formed from its component ions at temperatures below 90° C were in a state of supersaturation relative to solutions equilibrated with hydroxyapatite that had been formed at temperatures above 90°C.

Rootare et al. (1962) reported wide variations in the calculated ion-activity products for hydroxyapatite in solutions equilibrated with several commercial and laboratory-prepared samples of hydroxyapatite. They explained their results by postulating that $Ca_2(HPO_4)(OH)_2$ forms on

the surface of the hydroxyapatite and that the solution equilibrates with this surface complex and not with the hydroxyapatite. On the basis of the phase diagram for the $CaO-P_2O_5-H_2O$ system, Gray et al. (1962) postulated that the solution is in equilibrium with a surface phase of dibasic calcium phosphate dihydrate, $CaHPO_4 \cdot 2H_2O$, when hydroxyapatite is equilibrated in an acid buffer. Gray and Francis (1963) presented tabulated solubility data on enamel, dentin, bone, and synthetic hydroxyapatite in support of this concept. Moreno et al. (1968) and Wier (1968) obtained results that did not agree with the surface-complex concept.

Wier (1968) introduced a new hypothesis, that of the activity concept. According to this theory, hydroxyapatite solid may have different activities, each of which has a solubility-product constant. A range of values for the solubility-product constant may thus be obtained, depending on the activity of the solid with which the solution is in equilibrium. He obtained certain evidence in support of this hypothesis.

Kalpage (1954) was the first to suggest that the phosphatic component of Gafsa phosphate rock has a fixed solubility relationship in dilute hydrochloric acid. He represented his results by the following equation:

$$2\ pH - (3/2)\ pCa - pH_2PO_4 = 1.8,$$

where pCa and pH_2PO_4 are the negative logarithms of the activities of the calcium and dihydrogen phosphate ions, respectively. Peaslee (1960) worked on Florida phosphate rock and also found that the phosphatic component had a fixed solubility relationship, although he did not calculate what it was.

Chaverri (1962) applied the solubility-product principle in an

investigation of the dissolution of finely ground Florida phosphate rock under various conditions of weight of solid, concentration of acid, period of equilibration, and procedural technique. He assumed that the apatite in the sample was hydroxyfluorapatite with the formula $Ca_{10}(PO_4)_6(OH)_{2-x}F_x$, where $0 \leqslant x \leqslant 2$. An ionic-activity plot of (pH_2PO_4 + ½ pCa) against (pH - ½ pCa) showed that the results could not be expressed as a straight line but that there was a tendency for displacement of the experimental values from the hydroxyapatite line toward the fluorapatite + fluorite line with an increase in ratio of concentration of hydrochloric acid to weight of sample and for enhancement of the displacement in successive equilibrations. He proposed the hypothesis that the treatment with acid caused alteration of the surface of the hydroxyfluorapatite of the phosphate rock in the direction of fluorapatite by a process involving reaction of dissolved hydroxyl ions with hydrogen ions of the acid and by subsequent interaction of dissolved fluoride ions with the residual solid to enrich the surface layer with fluoride at the expense of hydroxyl.

Fassbender et al. (1966) investigated the solubility of hydroxyapatite and some phosphate rocks. They found that the quantity (5 pCa + 3 pPO_4 + pOH) was pH-dependent for all the phosphate investigated. The quantity increased with decreasing pH.

Wier (1968) studied the solubility of various phosphate rocks and suggested that the observed tendency of solutions in contact with phosphate rocks to become supersaturated with respect to fluorapatite may be a consequence of a reaction of foreign substances with the apatite constituent. He equilibrated an extract of a peat soil with hydroxyapatite and fluorite and found that the solids decolorized the solution

by adsorbing the organic matter. The solutions remained supersaturated with respect to fluorapatite after 96 days at 25°C.

Wier (1968) did one experiment in which aqueous suspensions of four phosphate rocks and hydroxyapatite with solid fluorite had been boiled and then equilibrated at 25° C. After six days, the solutions in contact with hydroxyapatite and three of the phosphate rocks exhibited ion-activity products equal to the solubility-product constant for fluorapatite. After 132 days of equilibration at 25° C, the solutions in contact with hydroxyapatite still had ion-activity products equal to the solubility-product constant for fluorapatite, but the solutions in contact with all the phosphate rocks were supersaturated with respect to fluorapatite. The results obtained with hydroxyapatite indicate that, in the presence of the fluoride ions supplied by the fluorite, at least the surface of the hydroxyapatite was transformed to fluorapatite. In explanation of the results with the phosphate rocks, Wier suggested that ions or other substances foreign to fluorapatite and hydroxyapatite may affect the equilibrium between the solid phase and the aqueous solution.

Agronomic Studies

Many experiments indicate that phosphate rock is of value only on acid soils. As a rule, liming acid soils reduces the effectiveness of phosphate rock as a source of phosphorus for plants. DeTurk (1942), however, emphasized the use of enough limestone with phosphate rock to take care of the needs of the legume in the crop rotation. Haugebak (1947) observed that legumes such as sweet clover have an exceptional capability to utilize the phosphorus of phosphate rock. As a result of

his review of the literature on long-term residual effects of phosphate rock, he stated that sweet clover gave greater increases in yield from phosphate rock than from superphosphate where the two sources of phosphorus were used in quantities of equal money value. The legumes generally respond well to applications of phosphate rock. The cereal grains and vegetable crops generally respond less well than the legumes and benefit from supplementary applications of more soluble phosphates.

Joos and Black (1951) found that the availability to plants of the phosphorus of phosphate rock was greater where the phosphate rock had been allowed to interact for some time with acid bentonite than where the plants were grown directly after the addition of the phosphate rock to the bentonite. This observation indicates that the chemical interaction of the phosphate rock with the bentonite increased the availability of the phosphorus of the phosphate rock. They found that the increase in availability due to the incubation period became smaller as the acidity of the bentonite was decreased.

Although it was considered from some early work that organic matter enhances the availability of the phosphorus of phosphate rock, Truog (1916) found that the solvent action of decaying organic residues on phosphate rock was of minor importance. In an investigation of the weathering of phosphate rock by different hydrogen-saturated colloidal systems, Graham (1955) found that the weathering ability of the various colloidal materials was in the following order: Amberlite IR-120 cation-exchange resin > Wyoming bentonite > Putnam clay > kaolinite > "humus."

In experiments in the greenhouse in which the response of plants to additions of different phosphate rocks was determined under otherwise

uniform conditions, Bartholomew (1935) found that the phosphate rocks lowest in fluorine gave the highest yields of the test plants. Bennet et al. (1957), however, found that the efficiency of phosphate rocks as phosphorus fertilizers was independent of their fluorine content.

Caro and Hill (1956) treated three acid soils with various phosphate rocks and grew alfalfa as a test crop. They correlated the yields of the crop with the results of different laboratory measurements of the properties of the phosphate rocks and found that the correlation coefficients were in the following order: bound carbon dioxide content > citric acid-soluble phosphorus > ammonium citrate-soluble phosphorus > particle density > particle weight > readily exchangeable phosphorus > surface area. Armiger and Fried (1957) found that the availability of the phosphorus of different phosphate rocks to plants was related to the specific surface, fluorine content, and carbonate content of the rocks.

Lehr and McClellan (1972) pointed out that the value of citrate-soluble phosphorus in phosphate rocks depends on the nature of the apatite in which the phosphorus occurs and not on the percentage content of phosphorus or apatite in the phosphate rock. They considered, therefore, that the practice of expressing the citrate-soluble phosphorus as a percentage of the total phosphorus does not provide a suitable solubility index. Instead, they proposed what they called the "absolute citrate solubility," which they defined as the ratio of the citrate-soluble phosphorus (determined by the procedure of the Association of Official Analytical Chemists) in per cent to the theoretical phosphorus content of the apatite mineral in the phosphate rock. The theoretical phosphorus content of the apatite mineral is estimated indirectly from an empirical

relationship they established between the chemical composition of the apatite and the X-ray diffraction pattern. The numerical values they obtained for the absolute citrate solubility ranged from near zero for unreactive apatites with composition approaching that of fluorapatite to a maximum of 23.6% for the most reactive apatite that had the highest degree of carbonate substitution. The levels of solubility indicated by the absolute citrate solubility indexes were well correlated with the apatite composition and with the response of various crops to additions of the phosphate rocks to soils as a source of phosphorus. They considered that phosphate rocks having absolute citrate soluble phosphorus values lower than 50 to 60% of the maximum value of 23.6% that they obtained with an Algeria phosphate rock were unsuitable for direct application as the sole source of phosphorus for growing crops.

MATERIALS AND METHODS

Hydroxyapatite

Preparation

The hydroxyapatite used was a commercial product obtained from the Mallinckrodt Chemical Works labeled as "calcium phosphate tribasic, $Ca_{10}(PO_4)_6(OH)_2$." This material contained some impurities of anhydrous dibasic calcium phosphate, $CaHPO_4$, as shown by the X-ray diffraction pattern (Figure 1) and by examination under the petrographic microscope.

To prepare the material for the first experiment, 1 kg of the solid was heated in an Erlenmeyer flask in a steam autoclave for 50 days at 120° C and a pressure of 1.05 kg per cm^2 with 5 liters of 1 N ammonium chloride solution. At intervals of 4 to 6 days, the suspension was filtered, and the solid was washed with fresh ammonium chloride solution, returned to the flask, treated with a volume of fresh ammonium chloride solution, and placed in the autoclave for further treatment. Finally the ammonium chloride was removed by washing with water, and the solid was dried at 105° C for 48 hours before use.

Characterization

The solid that had been treated with 1 N ammonium chloride solution had an X-ray diffraction pattern similar to the one given for hydroxyapatite by Lehr et al. (1967), as shown in Table 1. The impurity of anhydrous dibasic calcium phosphate was removed by the treatment, as indicated by the X-ray diffraction pattern in Figure 1. Additional tests showed that the solid was petrographically homogeneous, with a mean

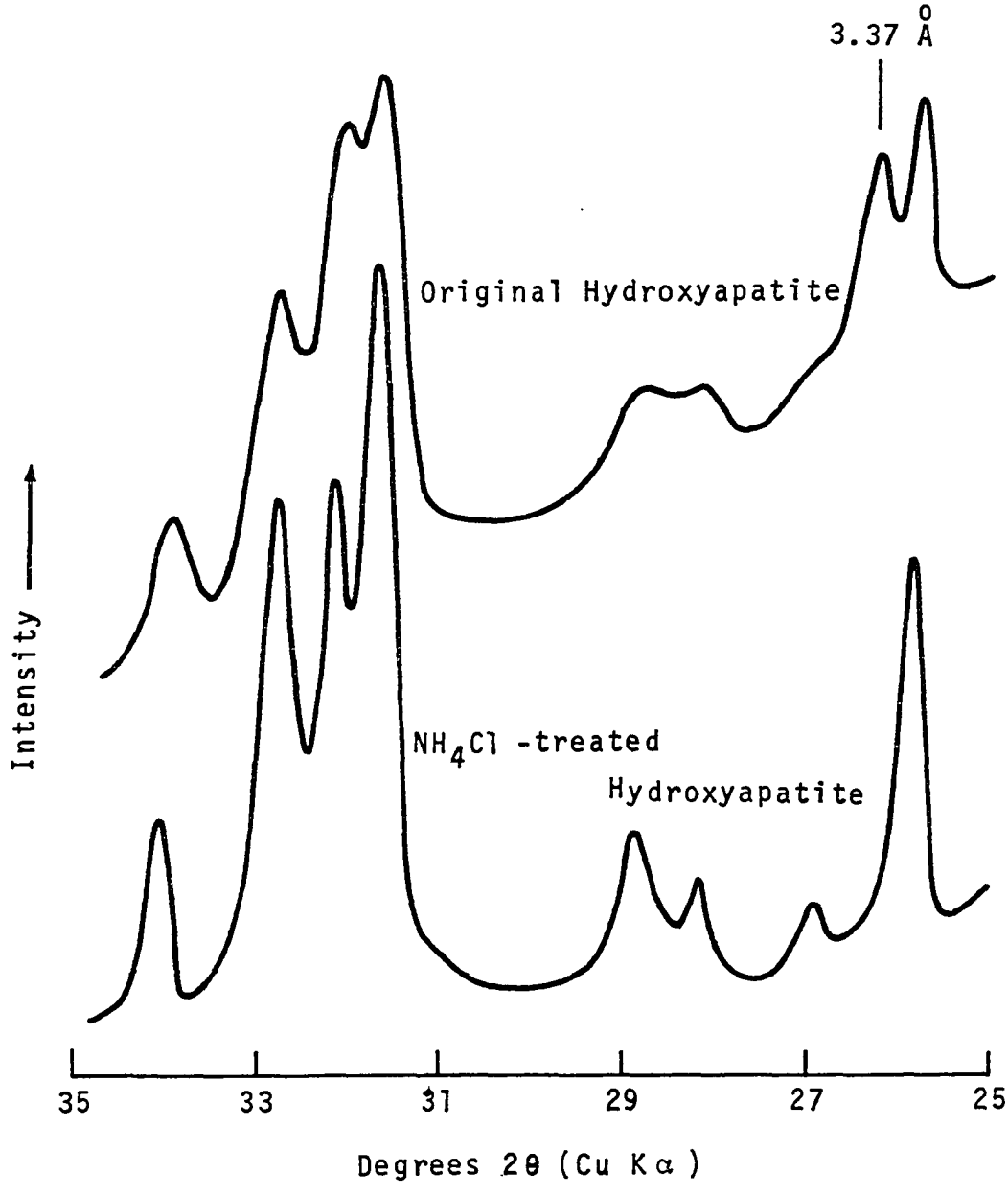

Figure 1. Smoothed X-ray diffraction patterns for original hydroxyapatite and NH_4Cl-treated hydroxyapatite. The peak at a d-spacing of 3.37 Å corresponds to the principal peak for anhydrous dibasic calcium phosphate

Table 1. X-ray diffraction data for NH_4Cl-treated hydroxyapatite, including peaks having relative intensities greater than 5 per cent within the range of d values from 2.06 to 8.17 Å, together with comparable data from Lehr et al. (1967)

Observed		Lehr et al. (1967)	
d,Å	Relative intensity	d,Å	Relative intensity
8.17	11	8.17	11
4.07	6	4.07	9
3.90	9	3.88	9
3.44	47	3.44	40
3.17	12	3.17	11
3.09	16	3.08	17
2.81	100	2.81	100
2.78	73	2.78	60
2.73	69	2.72	60
2.64	23	2.63	25
2.41	6	2.40	7
2.26	22	2.26	20
2.14	7	2.15	9
2.06	7	2.06	7

refractive index of 1.637 and a molar calcium-to-phosphorus ratio of 1.65 ± 0.01 (theoretical value = 1.67). No evidence of CO_2 gas formation was obtained when the solid was treated with dilute HCl.

Phosphate Rocks

Six phosphate rocks covering a wide range of carbonate substitution in the apatite component were used. All the samples except the Florida phosphate rock were kindly supplied by Dr. D. L. McCune, of the Tennessee Valley Authority, Muscle Shoals, Alabama. The Florida phosphate rock was a sample of commercial material sold for direct application by the American Cyanamid Company, New York. This sample is the same one used by Chaverri (1962). In Wier's (1968) work, this sample was designated as

Florida phosphate rock No. 1. More than 98% of the sample passed a 100-mesh sieve. All the TVA samples were uniformly sized at 70% through a 200-mesh sieve. The sources of the phosphate rocks are given in Table 2.

Table 2. Sources and types of phosphate rocks used in the experiments

Sample designation	Source of sample	Type of phosphate rock
Florida	Florida	Sedimentary
MR-465	Idaho	Sedimentary
MR-467	North Carolina	Sedimentary
MR-468	Tennessee	Sedimentary
MR-469	India	Metamorphic
MR-505	Missouri	Igneous

Citrate extraction

According to Smith and Lehr (1966), many phosphate rocks contain mechanically inseparable alkaline-earth carbonates (e.g., calcite and dolomite). As will be shown later, alkaline-earth carbonates are a source of difficulty in measurements of the solubility of the associated apatites. Removal of the alkaline-earth carbonates was accomplished by the method of Smith and Lehr (1966), which involves extracting the phosphate rock with an ammonium citrate solution that dissolves the alkaline-earth carbonates but has a pH high enough to dissolve only negligible amounts of the apatite.

To remove the alkaline-earth carbonates, 1-g samples of phosphate rock were suspended in 100 ml of 0.5 M triammonium citrate solution (pH 8.1) and digested at 65° C for 4 hours with constant agitation, after which the mixtures were allowed to stand at room temperature for 18 hours.

The mixtures were then filtered, and the extracted samples were washed thoroughly with water and dried at 105° C. To determine whether the alkaline-earth carbonates were completely removed, the extracted samples were checked by X-ray diffraction, infrared absorption, and petrographic microscopy. If removal was not complete, the samples were extracted again according to the same procedure.

As an example to illustrate the effectiveness of the extraction procedure, Figure 2 shows the X-ray diffraction pattern of sample MR-505 before and after treatment. The untreated sample contained both calcite and dolomite, and the diffraction peaks for both these minerals disappeared as a result of the extraction with citrate. Sample MR-505 contained approximately 2.8% CO_2 as alkaline-earth carbonate, the highest percentage found in any of the samples used. Figure 3 shows the infrared absorption patterns for the same samples. The three absorption bands due to alkaline-earth carbonate disappeared as a result of the extraction with citrate.

Table 3 shows the results of tests of identification of alkaline-earth carbonates in all six phosphate rocks before and after the extraction with citrate. One may note that the samples of Florida, MR-468, and MR-469 phosphate rocks contained no alkaline-earth carbonates detectable by any of the three identification methods used. The carbonate found in these phosphate rocks, therefore, are assumed to be in the form of carbonate apatite.

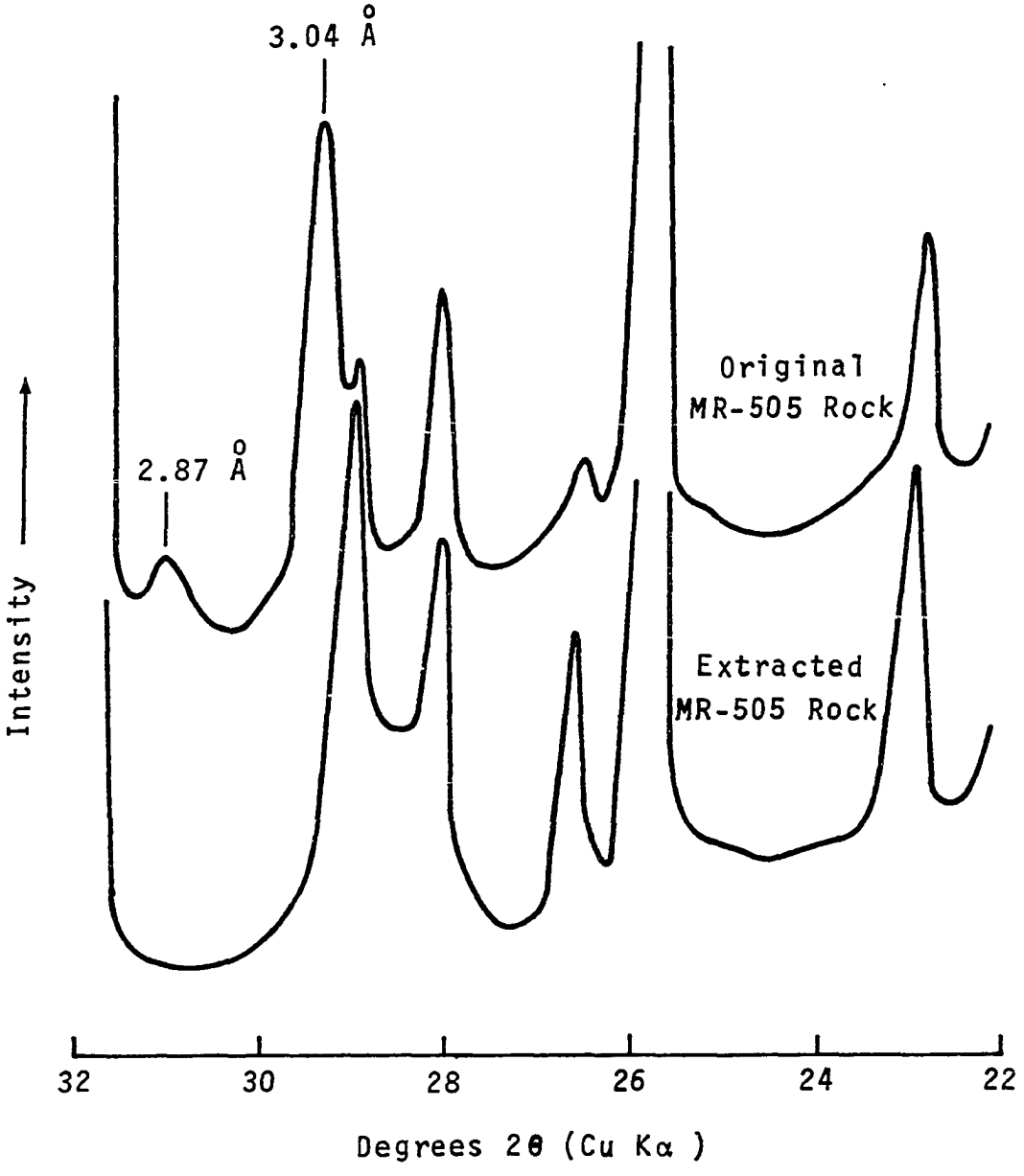

Figure 2. Smoothed X-ray diffraction patterns for MR-505 rock and citrate-extracted MR-505 rock. The peaks at d-spacings of 3.04 Å and 2.87 Å correspond to peaks for calcite and dolomite, respectively

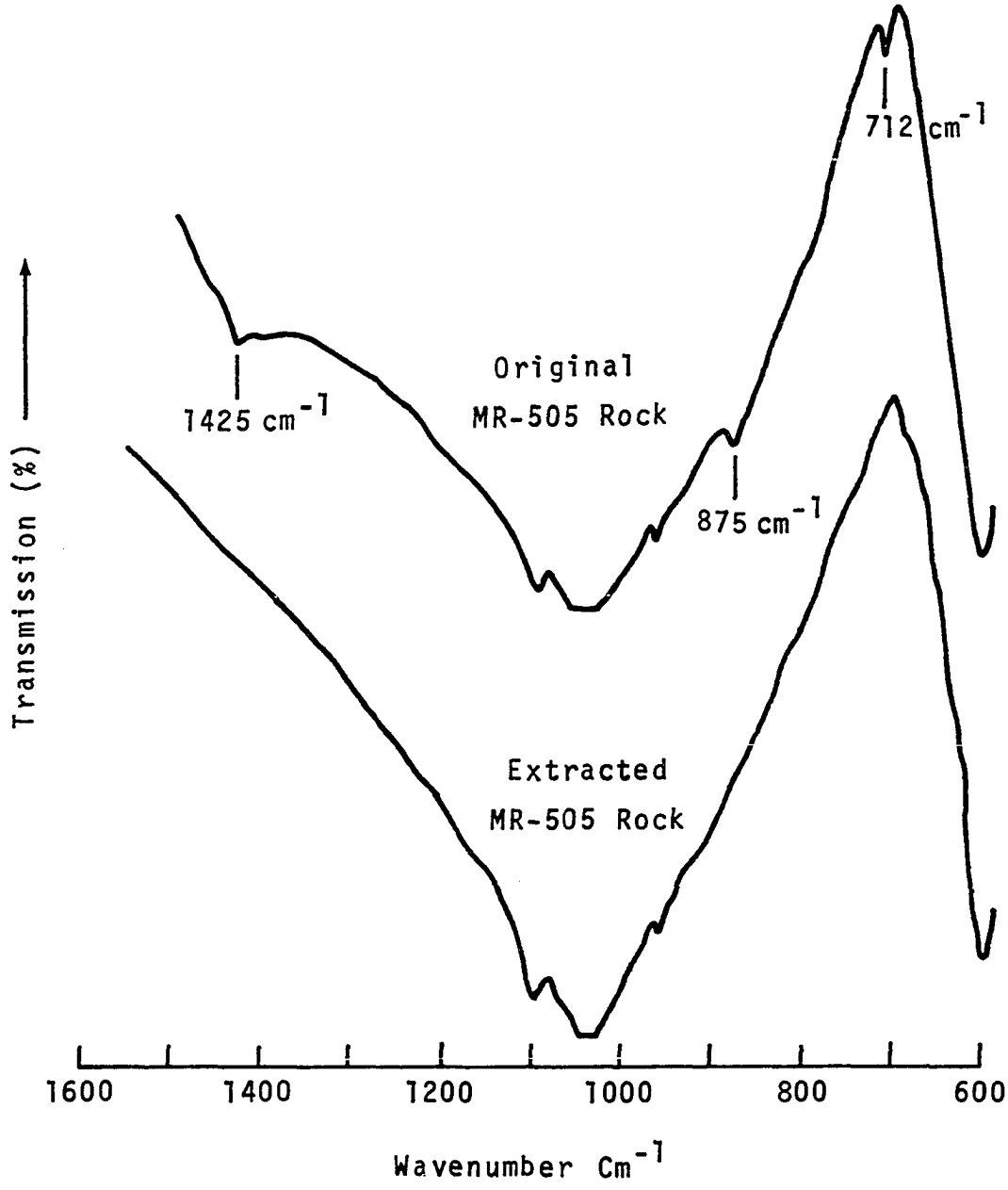

Figure 3. Smoothed infrared absorption patterns for MR-505 rock and citrate-extracted MR-505 rock. The absorption bands at 1425 cm^{-1}, 875 cm^{-1}, and 712 cm^{-1} correspond to those of alkaline-earth carbonates

Table 3. Identification of alkaline-earth carbonate in phosphate rocks before and after extraction with 0.5 M ammonium citrate solution at pH 8.1

Sample	Treatment	Presence of alkaline-earth carbonates[a]		
		X-ray diffraction	Infrared absorption	Petrographic microscope
Florida	None	N.D.	N.D.	N.D.
	Citrate-extracted	N.D.	N.D.	N.D.
MR-465	None	*	*	N.D.
	Citrate-extracted	N.D.	N.D.	N.D.
MR-467	None	*	N.D.	*
	Citrate-extracted	N.D.	N.D.	N.D.
MR-468	None	N.D.	N.D.	N.D.
	Citrate-extracted	N.D.	N.D.	N.D.
MR-469	None	N.D.	N.D.	N.D.
	Citrate-extracted	N.D.	N.D.	N.D.
MR-505	None	**	**	**
	Citrate-extracted	N.D.	N.D.	N.D.

[a] N.D. = not detected, * = small amount, ** = abundant.

Chemical characterization

Although more than 25 elements have been reported in igneous and metamorphic apatites, the composition of sedimentary apatites can be closely approximated by their contents of calcium, sodium, magnesium, phosphate, fluoride, and carbonate (Lehr et al., 1971). To determine the composition of the apatite portion of the samples without undue error from the contribution of minor amounts of clays, feldspars, and other accessory minerals sometimes present, the citrate-extracted samples were dissolved rapidly in warm 3 N HCl, and the filtrates were analyzed for the acid-soluble

constituents. Determination of CO_2, however, required treatment of the entire sample. The composition of the six apatites in terms of these major constituents is shown in Table 4. Two sources of error in this methods of estimating the chemical composition of the apatite fraction are the fluorite and clays present in some samples of phosphate rock. These substances are not extracted by the citrate solution, but they may contribute to the 3 N HCl solution.

Table 4. Dilute-acid-soluble components of citrate-extracted phosphate rocks[a]

Phosphate rock	Content of dilute-acid-soluble constituents, %[b]						Sum of constituents, %
	CaO	P_2O_5	F	CO_2	MgO	Na_2O	
Florida	45.7	31.0	3.4	3.6	0.62	0.25	84.6
MR-465	46.8	32.8	3.4	1.8	0.18	0.95	85.9
MR-467	48.2	30.3	3.6	5.0	0.50	1.04	88.6
MR-468	43.1	30.7	3.2	1.5	0.23	0.31	79.0
MR-469	54.3	40.2	3.6	0.7	0.02	0.12	98.9
MR-505	49.0	36.3	3.5	0.2	0.53	0.28	89.8

[a]All the data except those for Florida phosphate rock were provided by Lehr et al. (1971).

[b]Based on oven-dry weight of citrate-extracted phosphate rock.

Empirical composition of carbonate apatites

According to Lehr (1969), the empirical composition of carbonate apatite may be idealized as

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{2+0.4x}$$

They also developed the following relationship between the unit-cell

length, a_o, of the carbonate apatite and the chemical composition:

$$a_o = 9.374 - \frac{0.204\ x}{6 - x} \quad (1)$$

where 9.374 Å is the unit-cell length of pure fluorapatite without any isomorphous substitution.

The following equations are used to determine the moles of sodium, magnesium, and calcium per mole of carbonate apatite from equation 1:

$$Na_a = \frac{1.327\ x}{6 - x} \quad (2)$$

$$Mg_b = \frac{0.515\ x}{6 - x} \quad (3)$$

$$Ca_{10-a-b} = 10 - a - b \quad (4)$$

The value of a_o for the Florida phosphate rock was obtained by determining the d-spacings of the X-ray diffraction peaks and using this information in a computer program kindly supplied by Mr. J. R. Lehr, Tennessee Valley Authority, Muscle Shoals, Alabama. The program is shown in Appendix A. The a_o values for the other phosphate rocks were supplied by Mr. Lehr. The empirical formula of each carbonate apatite was determined by solving equations 1 through 4 with the value of a_o determined experimentally. Table 5 shows the unit cell length of the various apatites and their empirical formula.

Methods of Analysis

Calcium, sodium, and magnesium were determined with the aid of a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Lanthanum solution was used to prevent interference of phosphorus in the calcium determination. The instrument settings used were those recommended by the Perkin-Elmer Staff (1966).

Table 5. Unit-cell length, a_o of apatites determined by the X-ray diffraction technique and empirical formulas calculated therefrom

Phosphate rock	a_o, Å	Empirical formula
Florida	9.342	$Ca_{9.74}Na_{0.21}Mg_{0.05}(PO_4)_{5.19}(CO_3)_{0.81}F_{2.32}$
MR-465	9.356	$Ca_{9.83}Na_{0.12}Mg_{0.05}(PO_4)_{5.50}(CO_3)_{0.50}F_{2.20}$
MR-467	9.322	$Ca_{9.54}Na_{0.33}Mg_{0.13}(PO_4)_{4.80}(CO_3)_{1.20}F_{2.48}$
MR-468	9.357	$Ca_{9.85}Na_{0.11}Mg_{0.04}(PO_4)_{5.56}(CO_3)_{0.44}F_{2.18}$
MR-469	9.365	$Ca_{9.93}Na_{0.05}Mg_{0.02}(PO_4)_{5.77}(CO_3)_{0.23}F_{2.09}$
MR-505	9.372	$Ca_{10}(PO_4)_6F_2$

Phosphorus was determined by the colorimetric method of Dickman and Bray (1940), as modified by Legg and Black (1955). Interference of fluoride in the determination was presented by addition of boric acid (Kurtz, 1942).

Measurements of pH were made with a Beckman pH meter, Model G, with a glass electrode and a saturated calomel electrode.

Fluoride was distilled from the 3 N HCl extract at 135° C by the method of Brewer (1965). The fluoride in the distillate was determined by the method of Megregian (1954) with the exception that an Evelyn Photoelectric Colorimeter with a 515 mμ filter was used instead of a Beckman Model B spectrophotometer with a wavelength setting of 527.5 mμ. The activity of fluoride ion in aqueous solutions that had been equilibrated with phosphate rocks was measured directly by use of a Beckman

fluoride electrode coupled with a saturated calomel electrode.

Carbonate was determined by adding HCl to the phosphate rocks, absorbing the evolved CO_2 in Ascarite, and weighing the ascarite (Kolthoff and Sandell, 1952). The activity of carbonate ion in solutions equilibrated with phosphate rocks was estimated on the basis of the assumption that the solutions were in equilibrium with the partial pressure of CO_2 in the air. The theoretical basis for the calculations is given in the section on theoretical background.

Equilibrations

Solubility determinations were made with the aid of Plexiglas dialysis cells fitted with a cellulose acetate dialyzing membrane. The solid was placed on one side of the membrane, solution was added to both sides, and solution was removed for analysis from the side containing no solid. All solutions contained 0.001 M $HgCl_2$ to prevent microbial activity. During equilibration, the cells were kept in continuous motion in an incubator-shaker at 25° C. In the first experiment, the cells were closed, and no air was passed through the incubator. The CO_2 present in the incubator was trapped in trays of NaOH. In other experiments, the cells were open to the air, and humidified air was passed through the incubator during equilibration. Additional details may be found in Wier's thesis (1968, pp. 21 to 23).

Calculations

Activity coefficients were estimated for Ca^{++}, Na^{+}, Mg^{++}, $H_2PO_4^{-}$, HPO_4^{--}, and PO_4^{---} by use of the Debye-Hückel equation as described by Bates (1964). Values used for the constants in the equation were those

given by Kielland (1937). Values used for the dissociation constants of phosphoric acid were those given by Farr (1950).

The total ionic strength of the solution was estimated as three times the sum of the concentrations of mercury and calcium. In almost all cases the pH was low enough so that essentially all the phosphate ions were monovalent.

Reduction of calcium activities due to formation of $CaH_2PO_4^+$ and $CaHPO_4^o$ ion-pairs in solution was taken into account with the aid of dissociation constants given by Davies and Hoyle (1953). An iterative computer program was used to obtain the final approximations. The program is shown in Appendix B.

Theoretically, each sparingly soluble crystalline calcium phosphate is characterized by a unique solubility-product constant at a particular temperature. Hydroxyapatite (HA) has the formula, $Ca_{10}(PO_4)_6(OH)_2$, and the expression for the solubility-product constant is

$$(a_{Ca^{++}})^{10}(a_{PO_4^{---}})^6(a_{OH^-})^2 = K_{HA} \qquad (5)$$

where $\underline{a}$ represents the activities of the ions in solution and K_{HA} represents the solubility-product constant of hydroxyapatite. It is customary to express activities and solubility-product constants in terms of their negative logarithms to the base 10 and to indicate this operation by the letter $\underline{p}$. Thus, operationally, $\underline{p}$ is defined by $p = -\log_{10}$. Performing this operation on equation 5 and, for simplicity, letting the symbol for each element or radical stand for the activity, the following relation is obtained:

$$10\ pCa + 6\ pPO_4 + 2\ pOH = pK_{HA} \qquad (6)$$

Similarly, carbonate apatite (CA) has the general formula, $Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{2+0.4x}$, and the expression for the solubility-product constant is

$$(10-a-b)\ pCa + a\ pNa + b\ pMg + (6-x)\ pPO_4 + x\ pCO_3 + (2+0.4x)\ pF = pK_{CA} \quad (7)$$

where K_{CA} stands for the solubility-product constant for the carbonate apatite in a particular phosphate rock.

Data from most of the experiments will be presented on graphs with pI as the ordinate and pH as the abscissa. pI stands for the negative logarithm of the ion-activity product. For hydroxyapatite, pI_{HA} represents the sum of (10 pCa + 6 pPO_4 + 2 pOH); for fluorapatite (FA), pI_{FA} represents the sum of (10 pCa + 6 pPO_4 + 2 pF); and for carbonate apatite, pI_{CA} represents the sum of [(10-a-b) pCa + a pNa + b pMg + (6-x) pPO_4 + x pCO_3 + (2 + 0.4x) pF]. In some instances, data will be presented in graphs of the phosphate potential (pH_2PO_4 + ½ pCa) against the lime potential (pH - ½ pCa). The applicability of the various diagrammatic representations of solubility relations of calcium phosphate has been discussed by Chaverri (1962), Chaverri and Black (1966), and Wier (1968).

THEORETICAL BACKGROUND

Estimation of Carbonate-Ion Activity in Solutions

The activity of the carbonate ion in solutions that had been equilibrated with phosphate rocks was estimated on the basis of the assumption that the carbon dioxide in the solution was at equilibrium with the carbon dioxide in the atmosphere.

The following reactions apply:

$$H_2O + CO_2(g) = H_2CO_3 \tag{8}$$

$$H_2CO_3 = H^+ + HCO_3^- \tag{9}$$

$$HCO_3^- = H^+ + HCO_3^- \tag{10}$$

At equilibrium, the following relations must hold for reactions 8, 9, and 10:

$$\mu_{H_2O} + \mu_{CO_2(g)} = \mu_{H_2CO_3} \tag{11a}$$

$$\frac{(a_{H^+})(a_{HCO_3^-})}{a_{H_2CO_3}} = K_1 \tag{11b}$$

$$\frac{(a_{H^+})(a_{CO_3^{--}})}{a_{HCO_3^-}} = K_2 \tag{11c}$$

where μ stands for the chemical potential of the compound specified, and K_1 and K_2 are the first and second dissociation constants of carbonic acid. The chemical potential, μ_i, can be expressed as

$$\mu_i = \mu_i^o + RT\ln a_i \tag{12}$$

where

μ_i = chemical potential of compound i

μ_i^o = standard chemical potential of compound i

R = gas constant

T = absolute temperature

a_i = activity of compound i

If equation 12 is substituted into equation 11a, with the simplifying approximation that the activity of water is unity because the solutions are so dilute, it is found that

$$\ln a_{H_2CO_3} = \ln a_{CO_2(g)} + \frac{1}{RT}(\mu^o_{H_2O} + \mu^o_{CO_2} - \mu^o_{H_2CO_3}) \qquad (13)$$

where $a_{CO_2(g)}$ is the partial pressure of carbon dioxide, P_{CO_2}, in atmospheric air. From equations 11b and 11c, the following equation holds:

$$a_{H_2CO_3} = \frac{(a_{H^+})^2 (a_{CO_3^{--}})}{K_1 K_2} \qquad (14)$$

Substituting equation 14 into equation 13 and rearranging the result,

$$\ln a_{CO_3^{--}} = \ln P_{CO_2(g)} + \frac{1}{RT}(\mu^o_{H_2O} + \mu^o_{CO_2} - \mu^o_{H_2CO_3}) + \ln K_1 K_2 - \ln(a_{H^+})^2 \qquad (15)$$

Changing to logarithms to the base 10 and multiplying both sides of the equation by -1,

$$pCO_3^{--} = pP_{CO_2} - \frac{1}{2.303\ RT}(\mu^o_{H_2O} + \mu^o_{CO_2} - \mu^o_{H_2CO_3}) + pK_1 + pK_2 - 2pH \qquad (16)$$

It can be seen that all terms except pH on the right side of equation 16 are constant at a specified temperature and at a constant partial pressure of carbon dioxide in the atmospheric air. The activity of carbonate ion in the solution is then a function of pH. The activity increases as the

pH increases in the solution.

The constants used in equation 16 are P_{CO_2} = 0.0003 atm., R = 1.99 x 10^{-3} Kcal/deg mole, and T = 298°K. The values for the standard chemical potentials are from Rossini et al. (1952): $\mu^{o}_{H_2O}$ =-56.96 Kcal/mole, $\mu^{o}_{CO_2}$ = -94.26 Kcal/mole, and $\mu^{o}_{H_2CO_3}$ = -149.00 Kcal/mole. The values for the dissociation constants are from Willard et al. (1956): $K_1 = 3.04 \times 10^{-7}$, $K_2 = 4.00 \times 10^{-11}$.

Equation 16 is then simplified to

$$pCO_3^{--} = 22.06 - 2\ pH \qquad (17)$$

Therefore, the activity of carbonate may be estimated directly from the pH by a simple linear equation that applies (a) if the solution is at equilibrium with the partial pressure of CO_2 in the air, (b) if the pressure is 1 atmosphere, and (c) if the temperature is 25° C.

Free Energy of Formation of Carbonate Apatite

Introduction

The free energy of formation of carbonate apatite represents the surface activity that controls the solubility of apatite in aqueous solutions. Therefore, measurements of the free energy of formation should reflect the solubility characteristics of carbonate apatites with various chemical compositions. The advantage of the solubility approach to obtaining data on the free energy of formation is that experimentally it involves a solution-precipitation process that would be expected to have some similarity to the processes that occur when phosphate rocks are applied to the soil. Furthermore, if the measured data on the free energy of formation are correct, one may calculate the heat of solution

and the entropy, from which can be predicted the solubility of carbonate apatite under various conditions, especially those of chemical composition and temperature.

Theory

Calculation of free energy of formation of carbonate apatite. If the chemical formula of carbonate apatite is $Ca_{10-a-b}Na_aMg_b(CO_3)_x(PO_4)_{6-x}F_{2+0.4x}$, the dissolution reaction may be represented as follows:

$$Ca_{10-a-b}Na_aMg_b(CO_3)_x(PO_4)_{6-x}F_{2+0.4x} \rightleftharpoons (10-a-b)Ca^{++} + a\ Na^{+} + b\ Mg^{++} + x\ CO_3^{--} + (6-x)\ PO_4^{---} + (2+0.4x)F^{-} \quad (18)$$

From reaction 18, the following relation holds:

$$\Delta G^{o}_{R} = (10-a-b)\ \Delta G^{o}_{f,Ca^{++}} + a\ \Delta G^{o}_{f,Na^{+}} + b\ \Delta G^{o}_{f,Mg^{++}} + x\ \Delta G^{o}_{f,CO_3^{--}} + (6-x)\ \Delta G^{o}_{f,PO_4^{---}} + (2+0.4x)\ \Delta G^{o}_{f,F^{-}} - \Delta G^{o}_{f,CA} \quad (19)$$

where

ΔG^{o}_{R} = Free energy change of reaction at 25° C.

ΔG^{o}_{f} = Free energy of formation at 25° C.

At equilibrium,

$$\Delta G^{o}_{R} = -RT \ln K_{CA} \quad (20)$$

where K_{CA} is the equilibrium constant (solubility-product constant) for carbonate apatite.

Substituting equation 20 into 19 and rearranging the result,

$$\Delta G^{o}_{f,CA} = (10-a-b)\ \Delta G^{o}_{f,Ca^{++}} + a\ \Delta G^{o}_{f,Na^{+}} + b\ \Delta G^{o}_{f,Mg^{++}} + x\ \Delta G^{o}_{f,CO_3^{--}} + (6-x)\ \Delta G^{o}_{f,PO_4^{---}} + (2+0.4x)\ \Delta G^{o}_{f,F^{-}} + RT\ln K_{CA} \quad (21)$$

Thus, the free energy of formation of any given carbonate apatite can be calculated provided that ΔG_f^o of all ions and the equilibrium constant, K_{CA}, are known. The required values of ΔG_f^o for all ions are given by Rossini et al. (1952). The equilibrium constant, K_{CA}, can be obtained from the solubility measurement.

Free energy of formation of carbonate apatite as a function of carbonate substitution for phosphate. The general formula for carbonate apatite may be idealized as

$$Ca_{10-a-b}\ Na_a\ Mg_b\ (PO_4)_{6-x}\ (CO_3)_x\ F_y\ F_2$$

on the assumptions that the basic substitution is CO_3 + F for PO_4 and Na + Mg for Ca. According to McClellan and Lehr (1969), the average value for y is 0.4x, the average value for b is 0.4a, and electroneutrality is preserved when a = x-y. The general formula then may be rewritten as

$$Ca_{10-0.84x}\ Na_{0.60x}\ Mg_{0.24x}\ (PO_4)_{6-x}\ (CO_3)_x\ F_{2+0.4x}$$

At equilibrium between solid carbonate apatite and the solution,

$$\Delta G^o_{f,CA} = (10-0.84x)\ \Delta G^o_{f,Ca^{++}} + 0.60x\ \Delta G^o_{f,Na^+} + 0.24x\ \Delta G^o_{f,Mg^{++}} + x\Delta G^o_{f,CO_3^{--}} + (6-x)\ \Delta G^o_{f,PO_4^{---}} + (2+0.4x)\ \Delta G^o_{f,F^-} + RT\ln K_{CA} \quad (22)$$

where

$\Delta G^o_{f,CA}$ = Free energy of formation of carbonate apatite.

K_{CA} = Equilibrium constant at temperature T°K.

and

$$K_{CA} = (a_{Ca^{++}})^{10-0.84x}(a_{Na^+})^{0.60x}(a_{Mg^{++}})^{0.24x}(a_{PO_4^{---}})^{6-x}(a_{CO_3^{--}})^x (a_{F^-})^{2+0.4x} \quad (23)$$

Equation 23 may be rearranged as follows:

$$K_{CA} = (a_{Ca^{++}})^{10}(a_{PO_4^{---}})^{6}(a_{F^-})^{2}(a_{Ca^{++}})^{-0.84x}(a_{Na^+})^{0.60x}(a_{Mg^{++}})^{0.24x}$$
$$(a_{PO_4^{---}})^{-x}(a_{CO_3^{--}})^{x}(a_{F^-})^{0.40x}$$
$$\therefore K_{CA} = K_{FA} \cdot F(x) \qquad (24)$$

where

K_{FA} = Solubility-product constant of pure fluorapatite.

$$F(x) = (a_{Ca^{++}})^{-0.84x}(a_{Na^+})^{0.60x}(a_{Mg^{++}})^{0.24x}(a_{PO_4^{---}})^{-x}(a_{CO_3^{--}})^{x}$$
$$(a_{F^-})^{0.40x}$$

Substituting equation 24 into 22 and rearranging the result,

$$\Delta G^{o}_{f,CA} = (10\Delta G^{o}_{f,Ca^{++}} + 6\Delta G^{o}_{f,PO_4^{---}} + 2\Delta G^{o}_{f,F^-} + RT\ln K_{FA})$$
$$- (0.84\Delta G^{o}_{f,Ca^{++}} - 0.60\Delta G^{o}_{f,Na^+} - 0.24\Delta G^{o}_{f,Mg^{++}} - \Delta G^{o}_{f,CO_3^{--}}$$
$$+ \Delta G^{o}_{f,PO_4^{---}} - 0.40\Delta G^{o}_{f,F^-})\, x + RT\ln F(x) \qquad (25)$$

The following thermodynamic data for 25° C are from Rossini et al. (1952):

$\Delta G^{o}_{f,Ca^{++}}$ = -132.18 Kcal/mole

$\Delta G^{o}_{f,Na^+}$ = -62.59 Kcal/mole

$\Delta G^{o}_{f,Mg^{++}}$ = -108.99 Kcal/mole

$\Delta G^{o}_{f,PO_4^{---}}$ = -245.10 Kcal/mole

$\Delta G^{o}_{f,CO_3^{--}}$ = -126.22 Kcal/mole

$\Delta G^{o}_{f,F^-}$ = -66.08 Kcal/mole

From work by McCann (1968), the value of K_{FA} at 25° C is

$$K_{FA} = 10^{-119.2}$$

With substitution of these numerical values, equation 25 simplifies to

$$\Delta G^{o}_{f,CA} = -3087.3 + 139.8x + RT\ln F(x) \quad (26)$$

Now,

$$RT\ln F(x) = RT[-0.84\ \ln(a_{Ca}{}^{++}) + 0.60\ \ln(a_{Na}{}^{+}) + 0.24\ \ln(a_{Mg}{}^{++}) + \ln(a_{CO_3}{}^{--}) - \ln(a_{PO_4}{}^{---}) + 0.40\ \ln(a_{F}{}^{-})]x \quad (27)$$

If dissolution of the carbonate apatite is stoichiometric and if electroneutrality is maintained at equilibrium,

$$RT\ln F(x) = RTkx \quad (28)$$

where

$$k = -0.84\ \ln(a_{Ca}{}^{++}) + 0.60\ \ln(a_{Na}{}^{+}) + 0.24\ \ln(a_{Mg}{}^{++}) + \ln(a_{CO_3}{}^{--}) - \ln(a_{PO_4}{}^{---}) + 0.40\ \ln(a_{F}{}^{-}) = \text{constant}$$

Substituting equation 28 into equation 27,

$$\Delta G^{o}_{f,CA} = -3087.3 + (139.8+RTk)x$$

Now $R = 1.99 \times 10^{-3}$ Kcal/deg. mole and $T = 298\ ^{o}K$.

$$\therefore\ \Delta G^{o}_{f,CA} = -3087.3 + (139.8+0.6k)x \quad (29)$$

Therefore, a plot of $\Delta G^{o}_{f,CA}$ against x, the number of moles of carbonate per mole of apatite, should yield a straight line with a slope of (139.8+0.6k) and an intercept of -3087.3 (Kcal) at x = 0, corresponding to pure fluorapatite. According to McClellan and Lehr (1969), the maximum replacement of $PO_4{}^{---}$ by $CO_3{}^{--}$ ions in carbonate apatite is approximately 24% which corresponds to the limiting substitution predicted by Pauling's critical ratio rule. Thus, the value of x ranges from 0 to (6)(0.24) = 1.44.

Equation 29 states that the free energy of formation of carbonate apatite decreases linearly with an increase in substitution of carbonate for phosphate. Thermodynamic theory thus predicts that substitution of carbonate for phosphate in the apatite structure will increase the solubility of the apatite.

EXPERIMENTS

Experiment 1. Solubility of Hydroxyapatite

Introduction

Most investigations of the solubility of hydroxyapatite *in vitro* have failed to yield a solubility-product constant, and analyses of aqueous solutions equilibrated with soils have not yielded solubility values corresponding to saturation of the solutions with hydroxyapatite. Clark (1955), however, found a constant value of 115.5 as the solubility-product constant for hydroxyapatite ($10pCa + 6pPO_4 + 2pOH$). Wier (1968) also reported a constant value of 116.6 where he used a relatively high ratio of solid solution ($\geq$ 0.5 g/100 ml). With a low ratio of solid to solution (0.1 g/100 ml), Wier was not able to obtain a constant value of the ion activity product for hydroxyapatite within the pH range of 3.5 to 6.0. As the pH of the solution increased, the ion activity product increased and approached the solubility-product constant of the systems with the higher ratios of solid to solution.

To explain his experimental results, Wier proposed that the solid hydroxyapatite had a range of activities, corresponding to a range of solubilities, and that the hydroxyapatite with higher activity dissolved preferentially. According to this hypothesis, the results with 0.5, 1, and 10 g of solid per 100 ml showed the same solubility because so little of the solid was dissolved that all the solutions were in equilibrium with substantially the same solid with high activity. The values obtained with 0.1 g of solid per 100 ml showed a solubility similar to that obtained with the greater quantities of solid because at high pH values

little of the solid dissolved at high pH values. At low pH values, where more of the solid with high activity was dissolved, the solutions were in equilibrium with a solid of lower activity, and consequently the ion-activity product was decreased.

The objective of this experiment was to determine whether the implications of the activity concept discussed in the preceding paragraph could be substantiated.

Procedure

The hydroxyapatite used had been treated repeatedly with NH_4Cl solution in an attempt to remove the impurities and the hydroxyapatite with high activity, if such were present. Quantities of 0.1 and 1 g of the solid were used per 100 ml of solution. The initial pH of the solution was adjusted by dilute HCl solution. No air was passed through the incubator, and the initial CO_2 in the incubator was trapped in trays of NaOH solution. The equilibration time was 28 days, and the temperature was 25° C.

Results and discussion

The results are given in Table 6 and Figure 4. Figure 4 indicates that the hydroxyapatite which had been treated with 1N NH_4Cl solution exhibited a solubility-product constant. The PI_{HA} values obtained are all in the range from 118.1 to 122.6 and show no significant trend with pH of the solution or with ratio of solid to solution.

The results of this experiment are consistent with the activity hypothesis, from which it would be predicted that, if the extractions with ammonium chloride had removed all the high-activity material and

Table 6. Negative logarithm of ionic concentrations, ionic activities, and ion-activity-product for NH_4Cl-treated hydroxyapatite equilibrated with dilute HCl solutions at 25° C for 28 days

Solid per 100 ml of solution, g	pH	p[Ca][a]	$p[P]_T$[b]	pCa	pPO_4	$10pCa + 6pPO_4 + 2pOH$
0.1	4.48	2.256	2.480	2.49	13.12	122.6
0.1	4.51	2.164	2.389	2.41	12.98	121.0
0.1	4.53	2.251	2.453	2.49	12.99	121.7
0.1	4.85	2.489	2.693	2.68	12.58	120.6
0.1	5.04	2.489	2.721	2.68	12.22	118.1
0.1	5.21	2.752	2.967	2.91	12.12	119.5
0.1	5.24	2.752	2.975	2.91	12.07	119.1
0.1	5.75	3.409	3.602	3.53	11.67	121.8
0.1	5.85	3.377	3.585	3.50	11.46	120.0
0.1	5.87	3.377	3.620	3.50	11.46	120.0
0.1	5.88	3.377	3.620	3.50	11.44	119.8
0.1	5.89	3.420	3.658	3.54	11.46	120.4
0.1	5.89	3.432	3.699	3.55	11.50	120.7
0.1	5.92	3.456	3.721	3.57	11.46	120.7
0.1	6.61	4.155	4.398	4.26	10.84	122.4
1.0	3.98	1.481	1.706	1.91	13.44	119.7
1.0	4.01	1.478	1.709	1.90	13.38	119.3
1.0	4.75	2.197	2.452	2.44	12.55	118.2
1.0	4.75	2.197	2.440	2.44	12.55	118.2
1.0	4.80	2.291	2.526	2.52	12.52	118.7
1.0	4.83	2.276	2.532	2.50	12.47	118.2
1.0	5.05	2.520	2.807	2.71	12.29	118.7
1.0	5.08	2.516	2.796	2.71	12.22	118.2
1.0	5.22	2.777	3.143	2.94	12.28	120.6
1.0	5.36	2.780	3.125	2.94	11.98	118.6
1.0	5.71	3.237	3.796	3.36	11.95	121.9
1.0	5.85	3.208	3.699	3.33	11.58	119.1
1.0	5.88	3.222	3.745	3.35	11.57	119.1
1.0	5.88	3.276	3.796	3.40	11.62	119.9
1.0	5.88	3.222	3.699	3.35	11.52	118.9
1.0	5.90	3.252	3.796	3.38	11.58	119.4
1.0	5.91	3.268	3.824	3.39	11.59	119.6
1.0	5.91	3.174	3.824	3.30	11.59	118.7
1.0	5.94	3.276	3.796	3.40	11.50	119.1
1.0	5.95	3.252	3.824	3.38	11.51	118.9
1.0	6.60	4.046	4.301	4.15	10.77	120.9
1.0	6.65	4.046	4.301	4.15	10.68	120.3

[a] p[Ca] = negative logarithm of calcium concentration.

[b] $p[P]_T$ = negative logarithm of total phosphorus concentration.

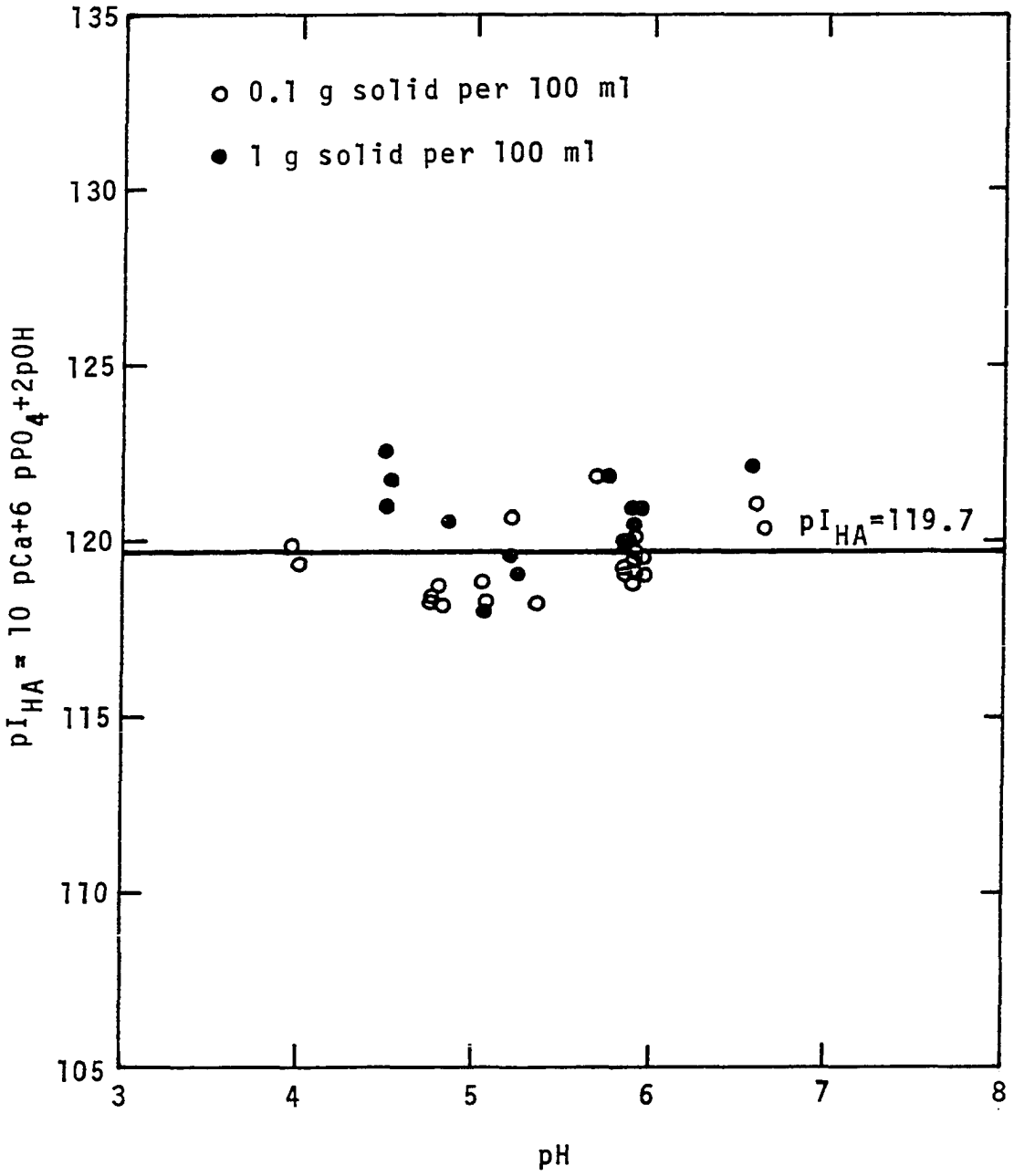

Figure 4. Plot of negative logarithm of ion activity product of hydroxyapatite versus pH of solutions obtained when two different quantities of NH_4Cl-treated hydroxyapatite were equilibrated with dilute HCl solutions for 28 days at 25° C. The horizontal line at pI_{HA} = 119.7 is the average of all the data and is taken as the solubility-product constant

had left only low-activity material, (a) the pI_{HA} values would not show a trend with pH with either 0.1 g or 1 g of solid hydroxyapatite per 100 ml of solution, (b) the pI_{HA} values would be the same with quantities of 0.1 and 1 g of solid hydroxyapatite per 100 ml, and (c) the pI_{HA} values would be higher than those obtained without the extraction to remove the high-activity material. The pK_{HA} value of 119.7 is the highest reported thus far, which indicates, according to the activity hypothesis, that the hydroxyapatite employed had a lower activity and hence was more stable than that used by other investigators.

Figure 5 permits a re-examination of some of Wier's data in the light of the results obtained with the NH_4Cl-extracted hydroxyapatite. At the low pH values, his pI_{HA} values agreed with the average pI_{HA} values for NH_4Cl-extracted hydroxyapatite, and at higher pH values they approached the average value of pI_{HA} = 116.6 that Wier obtained with additions of 0.5 g or more of nonextracted hydroxyapatite per 100 ml. These are the results that led to the activity hypothesis, and they are consistent with the hypothesis and with the results obtained with the NH_4Cl-extracted hydroxyapatie. At the low pH values, where a considerable portion of the solid hydroxyapatite was dissolved, the solid residue with which the solution was in equilibrium would have a low activity. At the high pH values, where little of the solid hydroxyapatite dissolved, the solution would be in equilibrium with a solid with higher activity and would show a greater ion activity product and a lower value of pI_{HA}.

To test the validity of the data for representing the solubility of hydroxyapatite, the negative logarithms of $(a_{Ca}{}^{++} \cdot a_{OH}^{2}{}^{-})$ and $(a_{H}^{3}{}^{+} \cdot a_{PO_4}{}^{---})$ in solution were calculated from Table 6 and plotted against each other in

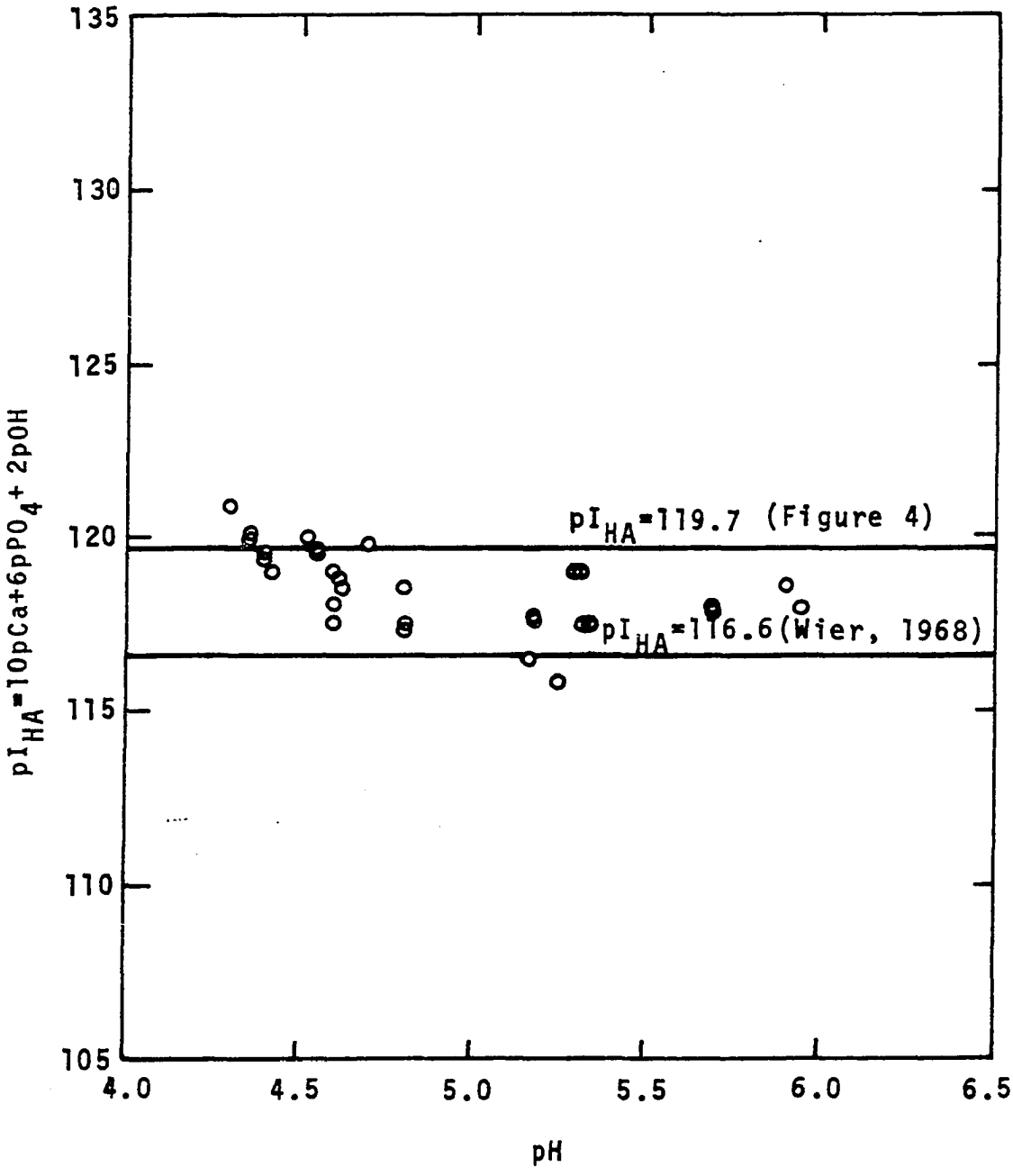

Figure 5. Plot of negative logarithm of ion activity product of hydroxyapatite versus pH of solutions obtained by Wier (1968) when he equilibrated 0.1-g quantities of nonextracted hydroxyapatite with 100-ml volumes of solutions at 25° C. The horizontal line at pI_{HA} = 116.6 represents the average value Wier obtained with additions of 0.5 g or more of nonextracted hydroxyapatite per 100 ml

Figure 6. Theoretically, if various solutions, each represented by a point on the graph, are in equilibrium with a solid crystalline calcium phosphate, the plots should be a straight line with a negative slope equal to the molar ratio of calcium to phosphorus in the crystalline phosphate (Moreno et al., 1968; Avnimelech et al., 1970). If the crystalline calcium phosphate is hydroxyapatite, therefore, the slope should be -1.67. The slope of the line shown in Figure 6 is -1.69, which is close to the theoretical value of -1.67. This observation indicates that the solid phase with which the solutions were equilibrating was hydroxyapatite.

Two other incidental observations made in the course of the investigation may be of some value in further work on the solubility of hydroxyapatite. First, the X-ray line-broadening technique was used on the 002 diffraction peak to see whether the differences in activity of the solid were correlated with crystalline size. No evidence of a difference in crystallite size was found in samples of hydroxyapatite from which different proportions of the original solid had been extracted. Second, the height of the X-ray diffraction peaks was increased when part of the solid was extracted, as shown in Figure 1. These observations suggest that part of original hydroxyapatite solid was amorphous to X-rays. That hydroxyapatite may exist in a form amorphous to X-rays is indicated by the finding (Beaton et al., 1963) that a good infrared absorption spectrum for hydroxyapatite was obtained from a preparation that did not yield an X-ray diffraction pattern.

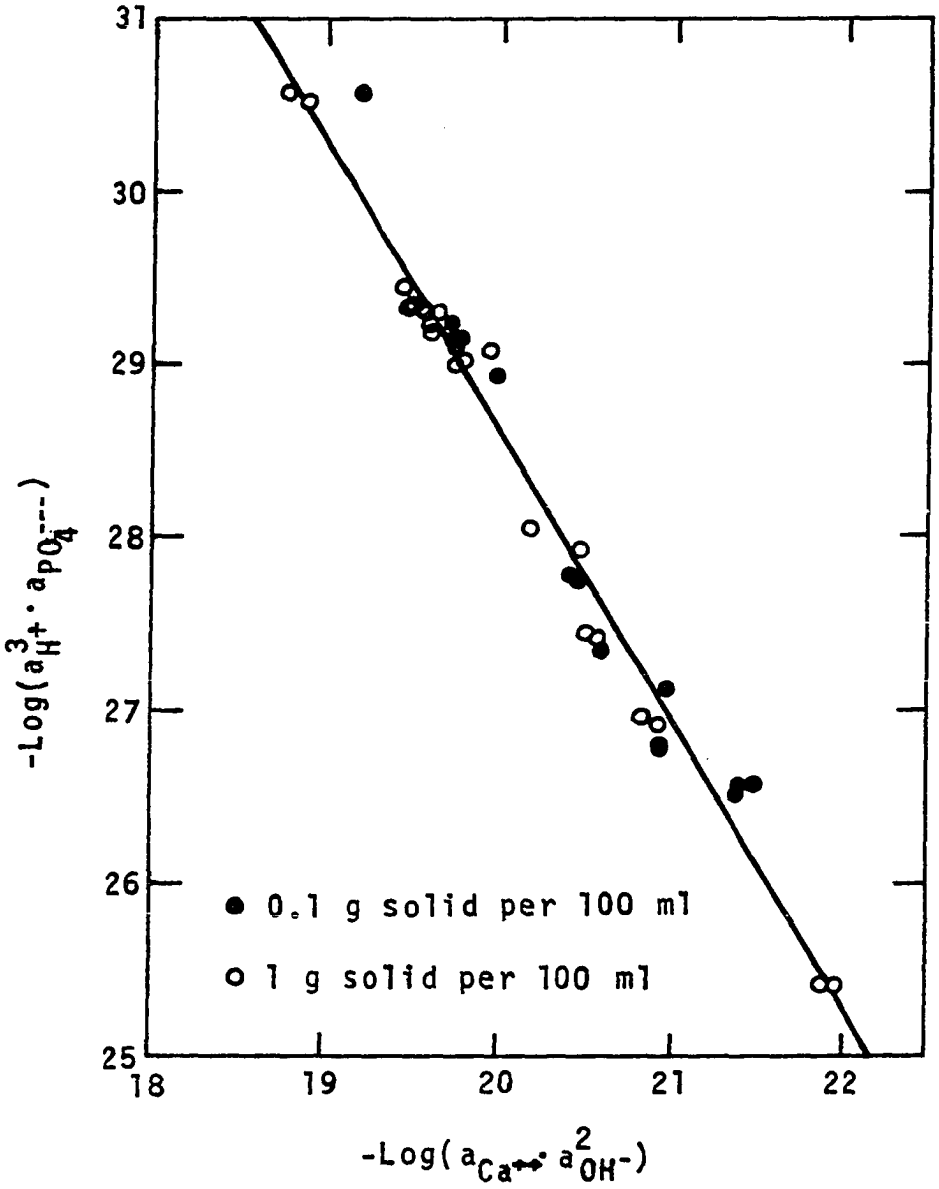

Figure 6. A plot of $-\log(a^3_{H^+} \cdot a_{PO_4^{---}})$ versus $-\log(a_{Ca^{++}} \cdot a^2_{OH^-})$ based on the chemical composition of solutions equilibrated with NH_4Cl-treated hydroxyapatite for 28 days at 25° C. Quantities of 0.1 and 1 g of hydroxyapatite were used per 100 ml of solution

Experiment 2. pH of Solution Equilibrated with Florida Phosphate Rock for Different Lengths of Time

Introduction

One criterion to determine whether an equilibrium has been attained between a solution and the phosphate rock with which it has been in contact is a stable pH of the solution. Dissolution of phosphate rock results in a change of pH in the solution. The objective of this experiment on change of pH with time was to obtain preliminary information on the time needed to attain equilibrium in investigations of the solubility of phosphate rock.

Procedure

Two 10-g samples of Florida phosphate rock were equilibrated with 100-ml volumes of solution containing 3 meq. of HCl at 25° C. The pH of the suspension was determined at frequent intervals at the beginning of the equilibration period and less frequently later on.

Results and discussion

Table 7 presents the results of the measurements of pH of the equilibrated solutions at intervals up to 74 days. Figure 7 shows a plot of the pH values against the time.

It can be seen from Figure 7 that the pH values remained within the range of 3.84 to 3.92 from 13 days onward. Dissolution of the phosphate rock thus ceased within 13 days. On the basis of this observation, the 30-day period of contact used in subsequent experiments should be long enough to permit attainment of an equilibrium in dissolution of phosphate rocks under similar conditions.

Table 7. pH of duplicate solutions after different times of equilibration of 10 g of Florida phosphate rock with 100 ml of solution containing 3 meq. of HCl at 25° C

Time in days	pH		Time in days	pH		Time in days	pH	
	Sample 1	Sample 2		Sample 1	Sample 2		Sample 1	Sample 2
1	3.35	3.28	13	3.88	3.86	41	3.90	3.86
3	3.62	3.60	17	3.86	3.84	58	3.88	3.88
6	3.68	3.71	23	3.89	3.87	70	3.90	3.90
9	3.72	3.74	30	3.87	3.87	74	3.92	3.90

Experiment 3. Solubility of Florida Phosphate Rock in the Presence of Fluorite After Boiling Followed by Equilibration at 25° C

Introduction

Rathje (1961) first observed the precipitation of hydroxyapatite with a decrease of pH through heating a solution saturated with calcium hydrogen phosphate. Chaverri (1962) also observed that the ionic concentrations of calcium and phosphorus and pH of the equilibrated solution in contact with Florida phosphate rock had decreased significantly after boiling followed by equilibration at 25° C for 5 days. These observations suggest that a new solid phase, possibly fluorapatite, formed upon boiling the equilibrated solution. The solubility data obtained by Chaverri, however, yielded a point that falls to the right of the fluorapatite plus fluorite line in the solubility diagram [plot of (pH_2PO_4 + 1/2 pCa) against (pH - 1/2 pCa)] in Figure 8. This finding indicates that the solution was supersaturated with respect to a solution in equilibrium with solid fluorapatite plus fluorite. Alternatively, fluorapatite may have been

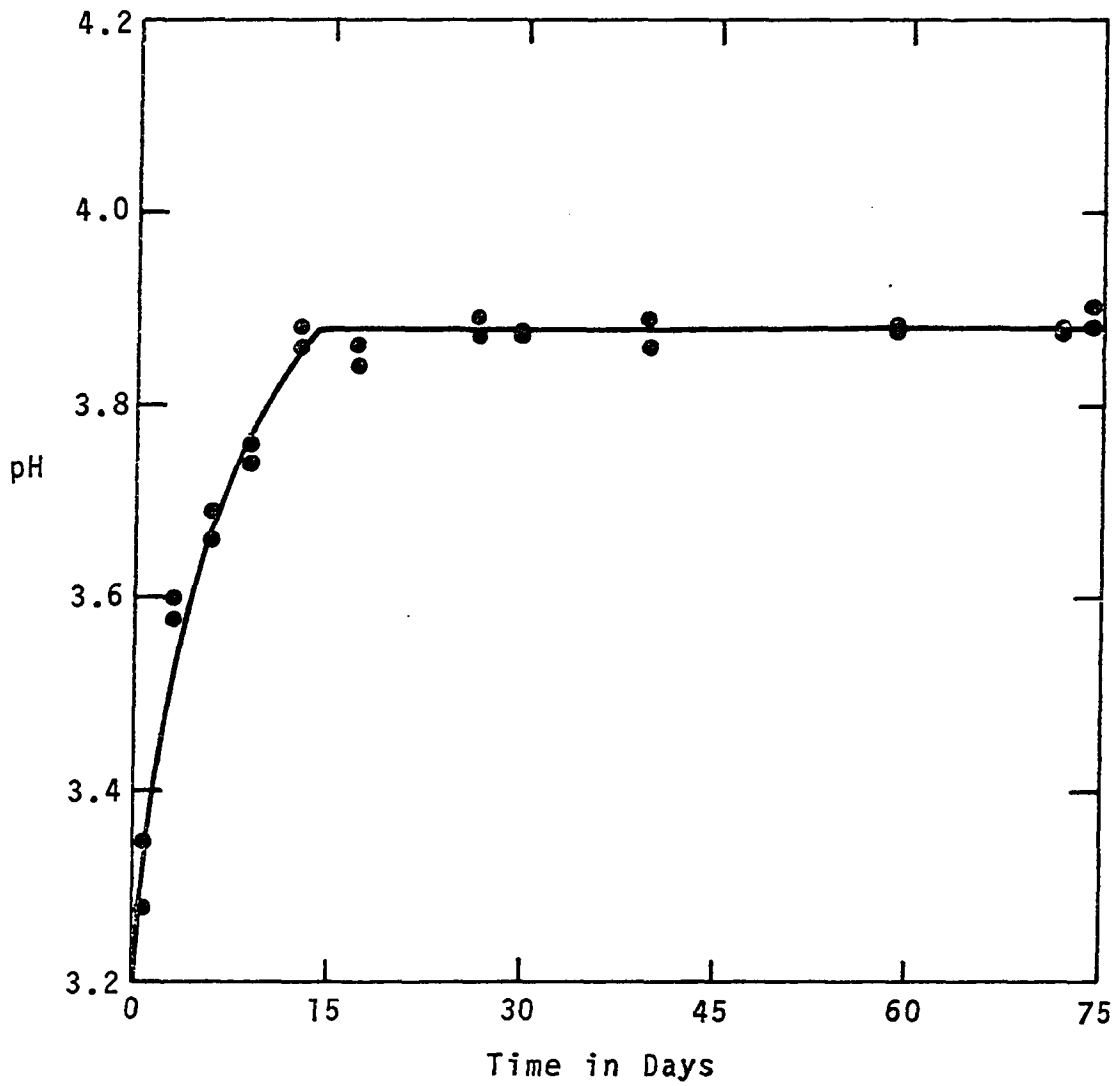

Figure 7. pH of duplicate solutions after different times of equilibration of Florida phosphate rock with a dilute HCl solution at 25° C

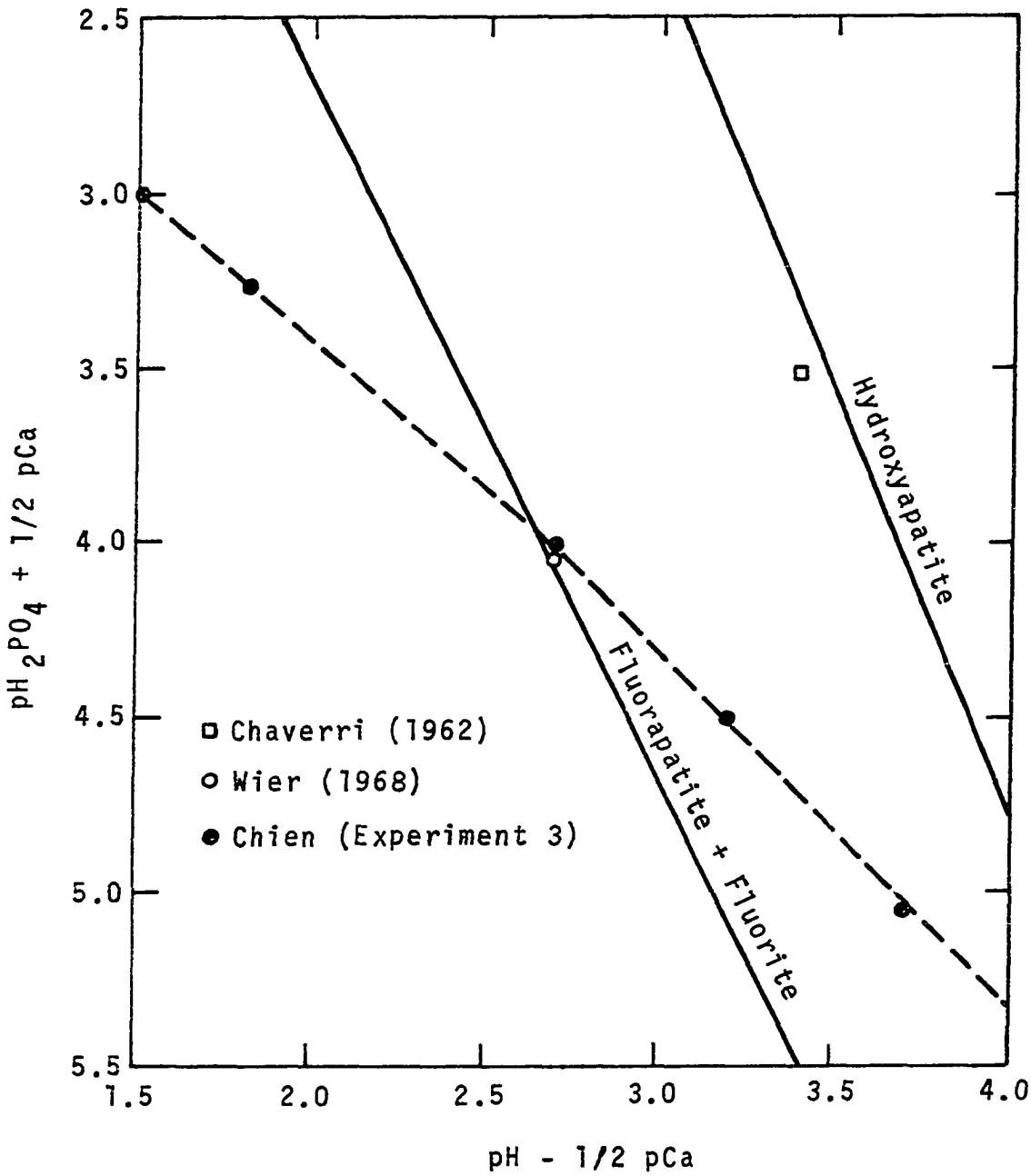

Figure 8. Solubilities exhibited by the solutions equilibrated with Florida phosphate rock in the presence of fluorite (Wier, 1968; Chien, Experiment 3) and absence of fluorite (Chaverri, 1962) after boiling followed by equilibration for 5 days at 25° C

formed in the absence of enough solid calcium fluoride to saturate the solution with calcium fluoride or fluorite.

Wier (1968) boiled a solution that had been equilibrated with the same Florida phosphate rock in the presence of added fluorite followed by equilibration at 25° C for 6 days. The data obtained by Wier yielded a point that falls on the fluorapatite plus fluorite line on the solubility diagram, as shown in Figure 8, which indicates that fluorapatite was precipitated when the solution was boiled.

The objective of this experiment was to determine whether fluorapatite would form upon boiling the solutions equilibrated with the same Florida phosphate rock and fluorite under conditions of a wide range of pH in the solutions.

Procedure

The solid to solution ratio used was 1 g of Florida phosphate rock and 0.25 g of fluorite per 100 ml of solution. The pH of the solution was adjusted by dilute HCl solution. The systems were boiled for 24 hours. Evaporation was limited by use of Liebig condensers. The systems were then equilibrated at 25° for 5 days in the 1-liter glass flasks in which they were boiled.

Analyses were made on the solution for calcium, phosphorus, and pH.

Results and discussion

The results are given in Table 8 and Figure 8. In Figure 8 the points moved from the right side of the fluorapatite plus fluorite line at high (pH - 1/2 pCa) values (indicating supersaturation of the solution) to the left side at low (pH - 1/2 pCa) values (indicating unsaturation of

Table 8. Negative logarithm of ionic concentrations, ionic activities, and phosphate and lime potentials of solutions after boiling with Florida phosphate rock plus fluorite followed by equilibration for 5 days at 25° C

Sample No.	pH	p[Ca]	$p[P]_T$	pCa	pH_2PO_4	pH_2PO_4+1/2pCa	pH-1/2pCa
1	2.48	1.542	1.755	1.94	2.03	3.00	1.51
2	2.86	1.748	2.046	2.09	2.23	3.27	1.82
3	3.95	2.291	2.665	2.50	2.74	4.00	2.70
4	4.60	2.638	3.055	2.79	3.11	4.50	3.21
5	5.18	2.863	3.521	2.98	3.56	5.05	3.69

the solution). The point representing sample 3 and the data obtained by Wier (1968) are almost on the fluorapatite plus fluorite line. The calculated average value of the negative logarithm of the ion-activity product of fluorapatite (10 pCa + 6 pPO_4 + 2 pF) for these two points was 118.5 on the assumption that the relation, pCa + 2 pF = 9.84, was valid. The value is in good agreement with Lindsay and Moreno's (1960) value of 118.5 for the negative logarithm of the solubility-product constant of fluorapatite.

Although the two points shown near the fluorapatite + fluorite line in Figure 8 suggest that fluorapatite formed upon boiling, the other points located to the right and left of the fluorapatite + fluorite line suggest that the occurrence of the two points near the line may be only a coincidence. Accordingly, further evidence is needed to verify that fluorapatite forms when the aqueous suspensions of phosphate rock are boiled.

With regard to the two points located to the left of the fluorapatite + fluorite line in Figure 8, it may be noted that the solubility of

Florida phosphate rock would be expected to be greater than that of fluorapatite because of the substitution of carbonate for phosphate. Nevertheless, the occurrence of the points to the left of the fluorapatite + fluorite line indicates that the solutions were unsaturated with respect to fluorapatite. Francis (1965) made a similar observation in experiments with fluorapatite. He suggested that the cause might be the development of a new solid phase of calcium fluoride on the surface of the apatite. The basis for his hypothesis was that the solubility of fluorapatite increases as the pH decreases. Calcium and fluoride are constituents of fluorapatite, and they are consequently released to the solution in increasing concentrations as the pH decreases. Eventually the solubility-product constant of calcium fluoride or fluorite is exceeded, a condition that should result in formation of solid calcium fluoride somewhere in the system. If the newly formed solid calcium fluoride should occur as a film on the surface of the apatite, the dissolution of the underlying apatite could conceivably be inhibited. Another possible explanation of the occurrence of the two points to the left of the fluorapatite + fluorite line in Figure 8 is that the solutions may have been supersaturated with respect to calcium fluoride and not saturated therewith, as assumed in the calculations.

Experiment 4. Effects of Fluorite and Calcium Carbonate on the Solubility of Florida Phosphate Rock

Introduction

Direct measurement of the activity of fluoride ion in aqueous solutions equilibrated with phosphate rock was considered impossible before the specific fluoride-ion electrode was developed. Fluoride forms soluble complexes with iron, aluminum, and silicon, and all these elements are present in phosphate rocks. Working on the same Florida phosphate rock used in the research described in this thesis, Chaverri (1962) and Wier (1968) made ion-activity-product calculations on the apatite constituent without estimating fluoride activity directly. They added fluorite (calcium fluoride) to the systems and assumed that the fluoride activity was fixed by the relation, $pCa + 2pF = 9.84$, which represents the negative logarithm of the solubility-product constant of fluorite at 25° C (Lindsay and Moreno, 1960). There are two disadvantages of having to rely on fluorite to fix fluoride activity. One is that fluorite is reported to reach the equilibrium very slowly (Farr and Elmore, 1962). The other is that, at low pH values, the solubility of apatites is much greater than that of fluorite, and the solutions tend to remain supersaturated with respect to fluorite (McCann, 1968). How well the fluoride activity is controlled by the solubility-product of fluorite is thus not certain.

The presence of carbonate and bicarbonate ions has been reported to affect the solubility of hydroxyapatite. Clark (1955) stated that he could not obtain a solubility-product constant for hydroxyapatite in the presence of atmospheric carbon dioxide. Olsen et al. (1960) reported

that the solubility of hydroxyapatite was greater in the presence of calcium carbonate than in its absence. The calculated values for 10pCa + $6pPO_4$ + 2pOH were 106.7 and 110.9 for solutions equilibrated with hydroxyapatite in the presence of calcium carbonate and in its absence, respectively. Since many sedimentary phosphate rocks contain a small but significant amount of alkaline-earth carbonates, it is important to investigate the effect of alkaline-earth carbonates on the solubility of phosphate rock.

The objective of this experiment was to investigate the effects of fluorite and calcium carbonate on the solubility of Florida phosphate rock. The fluoride-ion activity in the equilibrated solutions was measured directly with a specific fluoride-ion electrode. The results of the measurements were expected to provide a test of the validity of using fluorite to fix the fluoride-ion activity in solutions equilibrated with phosphate rock. The first part of this experiment was to calibrate the specific fluoride-ion electrode.

Procedure

A Beckman specific fluoride-ion electrode was used to measure the activity of fluoride ion in the solution. To calibrate the electrode, standard solutions were prepared with distilled water and sodium fluoride in concentrations of 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6} M. A saturated calomel electrode was used as the reference electrode coupled with the fluoride electrode. A Beckman pH meter was used to measure the resulting electrical potentials.

To study the effects of fluorite and calcium carbonate on the solu-

bility of phosphate rocks, seventeen samples of 1 g of Florida phosphate rock were used. A 0.25-g quantity of fluorite was added to each of eight samples, and 0.01 g of calcium carbonate was added to each of another three samples. The initial pH of the solutions was adjusted with dilute HCl solution. The equilibration period was 47 days for the samples of Florida phosphate rock alone and Florida phosphate rock plus fluorite. It was 33 days for the samples of Florida phosphate plus calcium carbonate.

Analyses of the solutions were made for calcium, phosphorus, pH, and pF. pF was measured by the specific fluoride-ion electrode after calibration.

Results and discussion

Because the fluoride activity in the reference solution in the electrode side of the crystal of lanthanum fluoride, LaF_3, is fixed, the overall response measured between a fluoride electrode and a reference electrode is

$$E = E_s - \frac{2.3RT}{F} \log a_{F^-} \qquad (30)$$

where

E = measured potential of fluoride electrode versus reference electrode,

E_s = fixed (or standard) portion of system potential due to choice of reference electrode and internal solution,

$\frac{2.3RT}{F}$ = Nernst factor, 59.1 m.v at 25° C (R and F are constants, T is the temperature in degrees Kelvin), and

a_{F^-} = fluoride-ion activity in the sample solution.

If pF is defined as $-\log a_{F^-}$, the following equation is obtained at

25° C,

$$E = E_s + 59.1 \text{ pF} \tag{31}$$

A plot of E versus pF, therefore, should yield a straight line with a slope of 59.1 m.v. and an intercept of E_s.

Since hydrofluoric acid is a weak acid (dissociation constant = 1.75×10^{-5} according to Willard et al., 1956), the activity of fluoride ion strongly depends on the pH of the solution. The following example shows how to calculate the fluoride activity from the fluoride concentration.

If the concentration of a standard solution of NaF is 10^{-2} M, the ionic strength (μ) of the solution is 0.01. The activity coefficient of fluoride ion, γ_{F^-}, can be estimated from the Debye-Hückel equation,

$$\log \gamma_i = -0.509 \, z_i^2 \sqrt{\mu}, \tag{32}$$

where γ_i is the activity coefficient of the i'th ion with electric charge Z. Thus, $\gamma_{F^-} = 0.89$ at $\mu = 0.01$.

Now

$$[HF] + [F^-] = [F]_T \tag{33}$$

$$\frac{a_{H^+} \cdot a_{F^-}}{a_{HF}} = 1.75 \times 10^{-5} \tag{34}$$

where $[HF]$, $[F^-]$, $[F]_T$, and a_{HF} are concentrations of undissociated hydrofluoric acid, fluoride ion, total fluoride, and activity of undissociated hydrofluoric acid, respectively.

Solving equations 33 and 34 for a_{F^-}, and noting that $a_{F^-} = \gamma_{F^-}[F^-]$ and $[HF] = a_{HF}$, we obtain,

$$a_{F^-} = \frac{1.75 \times 10^{-5} \times \gamma_{F^-} \times [F]_T / a_{H^+}}{\gamma_{F^-} + (1.75 \times 10^{-5} / a_{H^+})} \quad (35)$$

In the standard solutions of NaF, the pH value is greater than 6. Under these conditions $1.75 \times 10^{-5}/a_{H^+}$ in the denominator becomes much larger than γ_{F^-}, which has values <1. The equation thus simplifies to the following as a good approximation:

$$a_{F^-} = \gamma_{F^-}[F]_T \quad (36)$$

In the example, $[F]_T = 10^{-2}$ M and $\gamma_{F^-} = 0.89$. Thus, $a_{F^-} = 0.89 \times 10^{-2}$ M and pF = 2.05.

Potentials observed with the standard solutions of NaF, together with the calculated values of pF, are shown in Table 9. A plot of measured E versus pF is shown in Figure 9.

Table 9. Potentials (E) observed with standard fluoride solutions together with calculated values of pF

Concentration, M	Activity coefficient	Activity, M	pF	Observed E, millivolts
10^{-2}	0.89	0.89×10^{-2}	2.05	114
10^{-3}	0.96	0.96×10^{-3}	3.02	172
10^{-4}	0.99	0.99×10^{-4}	4.00	228
10^{-5}	1.00	1.00×10^{-5}	5.00	282
10^{-6}	1.00	1.00×10^{-6}	6.00	314

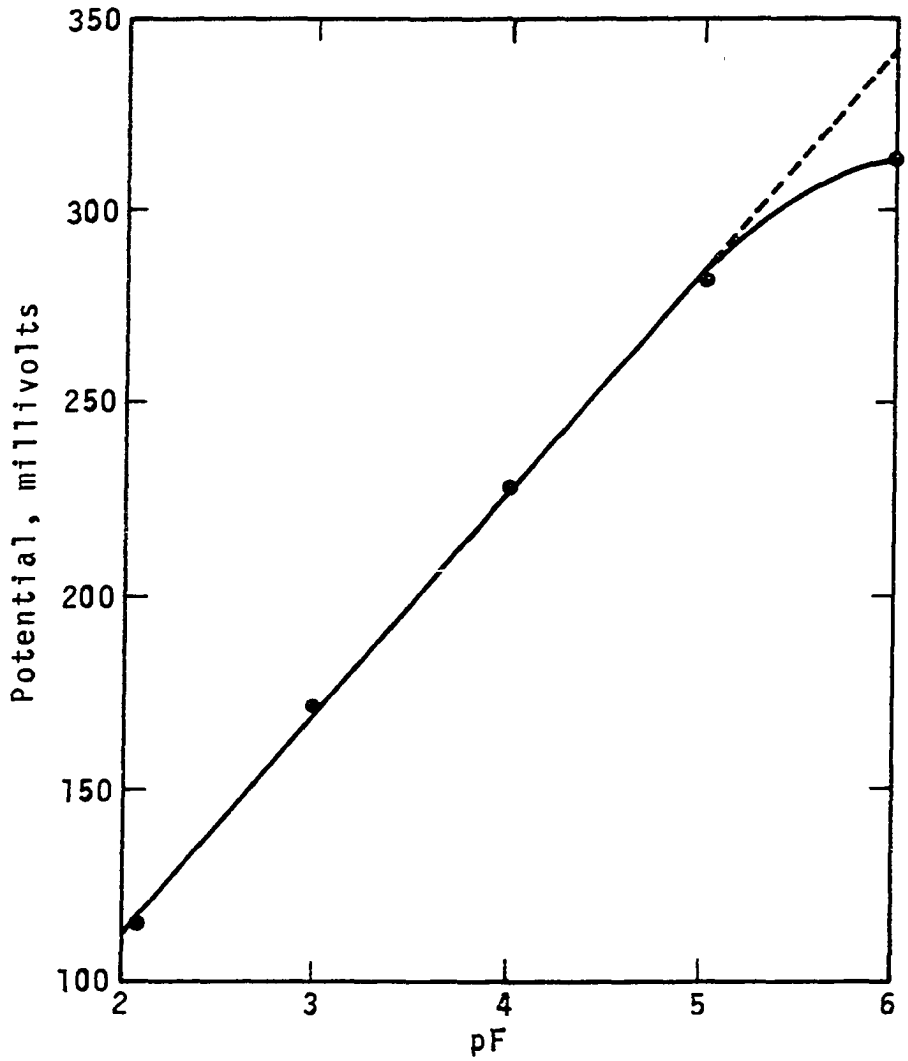

Figure 9. Plot of potentials measured with a Beckman specific fluoride-ion electrode at 25° C versus pF of standard fluoride solutions

Figure 9 shows that the measured E is a linear function of pF up to pF = 5.0. The slope of the straight line was calculated as 59.0 m.v., which is in good agreement with the theoretical value of 59.1 m.v. predicted in equation 31. The point at pF = 6 deviated from the straight line. Two reasons may be suggested to account for the deviation: (1) the fluoride electrode responds with an apparent preference of F^- over OH^- of only 10:1. Therefore, interference from the hydroxyl ion becomes more pronounced as fluoride activity decreases. (2) The actual fluoride activity may have exceeded the calculated activity. Wier (1968) reported that the fluoride concentration of the distilled water was approximately 3.3×10^{-7} M.

The effects of fluorite and calcium carbonate on the solubility of Florida phosphate rock at 25° C are shown in Table 10 and Figure 10. In Figure 10, the points shown in the solubility diagram moved from the supersaturated side of the fluorapatite plus fluorite line to the unsaturated side with a decrease in pH - $\frac{1}{2}$pCa. Addition of fluorite seemed to have no effect on the solubility. Addition of calcium carbonate, however, increased the apparent solubility of the phosphate rock at high pH - $\frac{1}{2}$pCa values. Further information on the effect of carbonates may be found in Appendix C.

To determine whether fluorite fixed the fluoride-ion activity, the negative logarithm of the ion-activity product of fluorite (pCa + 2pF) was calculated, with results as shown in Table 11 and Figure 11. The values of pF were obtained by measuring the fluoride-ion activity in the solutions with the aid of the fluoride electrode. In Figure 11, the points for systems with fluorite added at pH > 4.4 were close to the line

Table 10. Negative logarithm of ionic concentrations, ionic activities, and lime and phosphate potentials of solutions equilibrated at 25° C with Florida phosphate rock alone, Florida phosphate rock plus fluorite, and Florida phosphate rock plus calcium carbonate

Addition per[a] 100 ml of solution	pH	p[Ca]	$p[P]_T$	pCa	pH_2PO_4	$pH_2PO_4 + \frac{1}{2}pCa$	$pH - \frac{1}{2}pCa$
None	3.08	1.692	1.944	2.05	2.11	3.14	2.05
None	3.09	1.616	1.883	2.00	2.06	3.06	2.09
None	4.14	2.167	2.466	2.41	2.55	3.76	2.93
None	4.15	2.217	2.513	2.46	2.60	3.82	2.92
None	4.39	2.506	2.826	2.70	2.89	4.24	3.04
None	4.43	2.496	2.796	2.69	2.86	4.20	3.09
Fluorite, 0.25g	2.95	1.642	1.904	2.02	2.09	3.10	1.94
Fluorite, 0.25g	2.97	1.675	1.940	2.04	2.12	3.14	1.95
Fluorite, 0.25g	4.08	2.200	2.490	2.44	2.58	3.80	2.86
Fluorite, 0.25g	4.10	2.214	2.490	2.45	2.57	3.80	2.87
Fluorite, 0.25g	4.39	2.513	2.788	2.70	2.85	4.20	3.04
Fluorite, 0.25g	4.42	2.499	2.778	2.69	2.84	4.19	3.08
Fluorite, 0.25g	4.93	3.005	3.326	3.14	3.37	4.94	3.36
Fluorite, 0.25g	4.95	3.013	3.352	3.15	3.40	4.97	3.38
$CaCO_3$, 0.01g	2.99	1.731	2.026	2.07	2.20	3.23	1.95
$CaCO_3$, 0.01g	4.45	2.219	2.606	2.44	2.69	3.91	3.23
$CaCO_3$, 0.01g	5.24	2.503	3.035	2.67	3.10	4.44	3.90

[a] 1g of phosphate rock was present per 100 ml of solution in all cases.

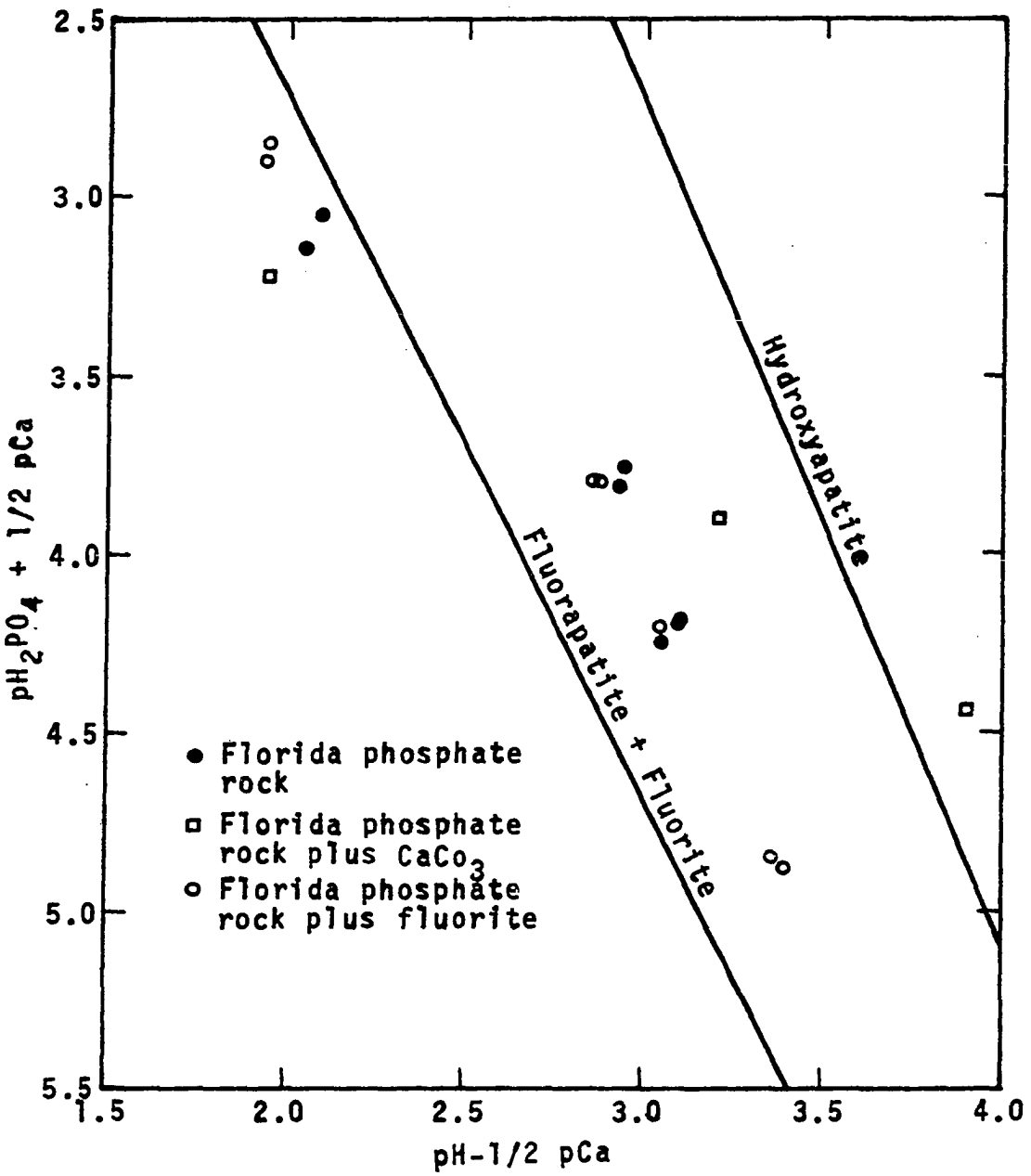

Figure 10. Solubility diagram showing a plot of $pH_2PO_4+\frac{1}{2}pCa$ against $pH-\frac{1}{2}pCa$ in solutions equilibrated at 25° C with Florida phosphate rock alone and with Florida phosphate rock plus fluorite or calcium carbonate

Table 11. Negative logarithms of ionic activities and ion-activity product for fluorite in solutions equilibrated with Florida phosphate rock in the presence and absence of fluorite for 47 days at 25° C

Addition per 100 ml[a] of solution	pH	pCa	pF	pCa + 2pF
None	3.08	2.05	3.55	9.15
None	3.09	2.00	3.55	9.10
None	4.14	2.41	3.65	9.75
None	4.15	2.46	3.65	9.76
None	4.39	2.70	3.87	10.40
None	4.43	2.79	3.85	10.45
Fluorite, 0.25g	2.95	2.02	3.58	9.18
Fluorite, 0.25g	2.97	2.04	3.55	9.13
Fluorite, 0.25g	4.08	2.44	3.60	9.64
Fluorite, 0.25g	4.10	2.45	3.65	9.65
Fluorite, 0.25g	4.39	2.70	3.55	9.80
Fluorite, 0.25g	4.42	2.69	3.60	9.90
Fluorite, 0.25g	4.93	3.14	3.35	9.84
Fluorite, 0.25g	4.95	3.15	3.37	9.89

[a]1g of phosphate rock was present per 100 ml of solution in all cases.

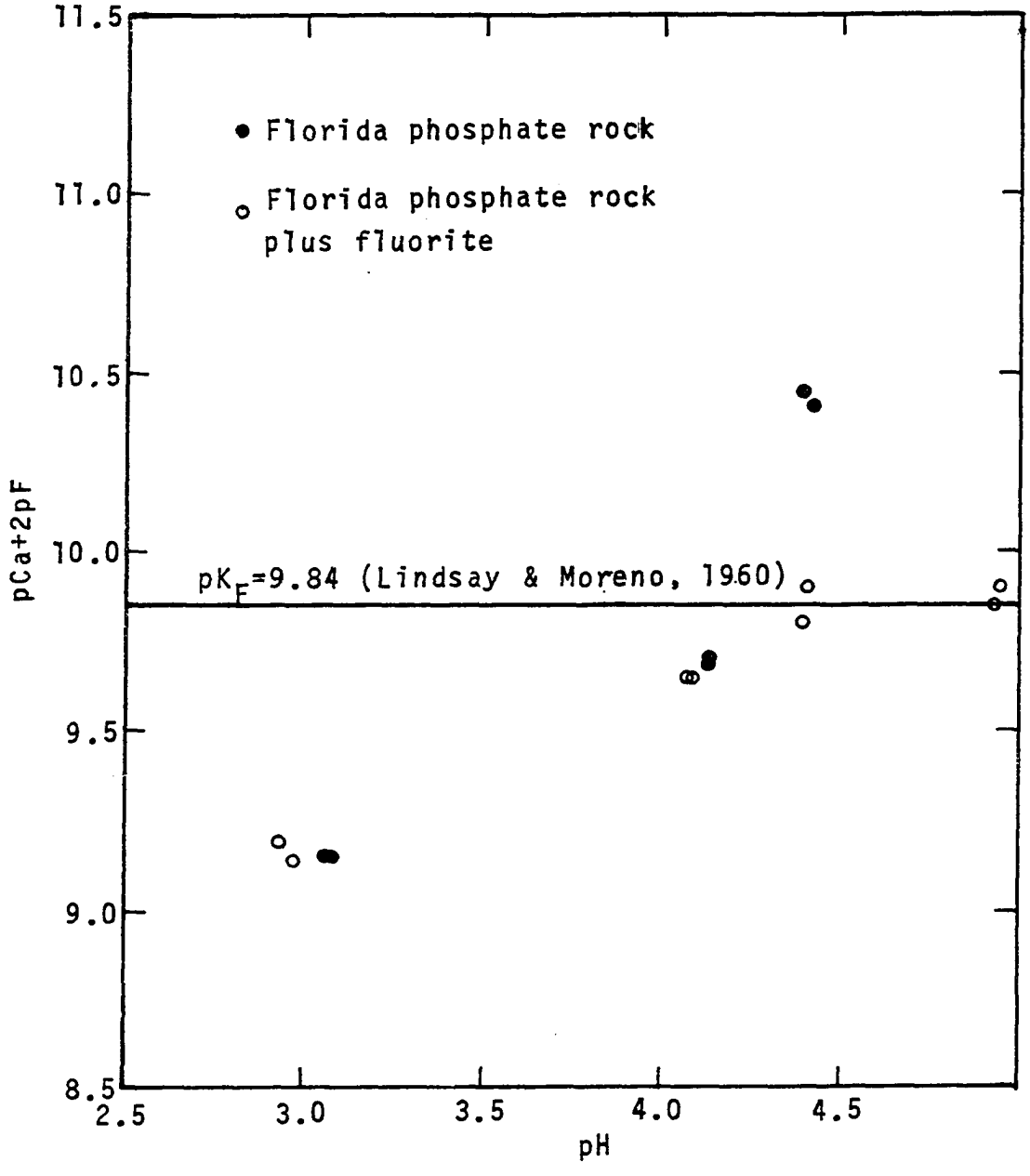

Figure 11. Negative logarithm of ion activity product of fluorite versus pH of solutions equilibrated with Florida phosphate rock in the presence and absence of fluorite for 47 days at 25° C

corresponding to the ion-activity product of solutions saturated with fluorite, indicating that the solutions were at equilibrium with solid fluorite. On the other hand, the points for systems without fluorite were above the line, indicating that the solutions were unsaturated with respect to solid fluorite at pH > 4.4. This observation indicates that the Florida phosphate rock did not contain enough fluorite to saturate the solution. At the lower pH values (pH < 4.4), the systems with and without fluorite were all supersaturated with respect to solid fluorite. The supersaturation at the low pH values may have developed in the following way: The solubility of the apatite mineral increases with decreasing pH, and calcium fluoride is produced in the dissolution process. The apatite is more soluble than calcium fluoride at low pH values (McCann, 1968). Calcium fluoride, however, precipitates slowly from supersaturated solutions (Jensen, 1937).

The results thus indicate that addition of fluorite did not control the fluoride-ion activity in solutions at the low pH values. The relation, $pCa + 2pF = 9.84$, therefore, was not valid where the pH values were below 4.4. Presumably the supersaturation would have disappeared, had the equilibration time been extended indefinitely.

Experiment 5. Test of Formation of Fluorapatite upon Boiling the Solutions Equilibrated with Florida Phosphate Rock

Introduction

Wier (1968) obtained evidence for formation of fluorapatite when suspensions of phosphate rock were boiled, but he did not have a fluoride electrode and based his inferences on the assumption that the fluorite

he added produced a solution saturated with fluorite. In the third experiment in this thesis, it was found that boiling suspensions of Florida phosphate rock in the presence of fluorite yielded points on the fluorapatite plus fluorite line in the solubility diagram. If the solutions were saturated with fluorite, these results indicate that boiling caused precipitation of fluorapatite. In the fourth experiment, however, it was found that solutions with pH values below 4.4 were supersaturated with fluorite. Possibly, therefore, the occurrence of the points near the line corresponding to a solution saturated with fluorapatite and fluorite was only a coincidence.

The objective of this experiment was to obtain further evidence on the formation of fluorapatite when suspensions of Florida phosphate rock were boiled. This experiment differed from the third experiment in that the fluoride-ion activity was measured by a specific fluoride electrode after boiling. In the third experiment, the fluoride-ion activity was inferred from the relation, $pCa + 2pF = 9.84$.

Procedure

The two samples of Florida phosphate rock used in the second experiment were used. The equilibration period was extended to 77 days. Then the solutions were boiled for 2 hours, after which they were equilibrated at 25° C. It took approximately 10 hours for the temperature of the solutions to decrease to 25° C. The equilibration period was then continued for another 67 days at 25° C after boiling. Analyses were made on the solutions before and after boiling for calcium, phosphorus, and pH. pF was measured only on the solutions after boiling.

Results and discussion

The results are given in Table 12 and Figure 12. In Figure 12, the two points which represented the solutions equilibrated with Florida phosphate rock for 10 hours after boiling are very close to the line corresponding to a solution saturated with fluorapatite but unsaturated with fluorite (pCa + 2pF = 11.30). This observation may indicate that the solutions were saturated with fluorapatite and unsaturated with fluorite. The values of ($10pCa + 6pPO_4 + 2pF$) in Table 13 for solutions after boiling followed by equilibration for 10 hours averaged 119.3, which is in good agreement with the value of 119.2 reported by McCann (1968) as the solubility-product constant for fluorapatite. The average value of (pCa + 2pF) for the same systems was calculated as 11.28. These findings verify the fluorapatite formed upon boiling the solutions equilibrated with Florida phosphate rock but that fluorite did not form. In Figure 12, the points which represent solutions equilibrated with phosphate rock without boiling or with boiling followed by equilibration for 67 days lie on the supersaturated side of a line representing solutions saturated with fluorapatite and unsaturated with fluorite (pCa + 2pF = 11.30). These findings suggest that the formation of fluorapatite upon boiling the solutions equilibrated with Florida phosphate rock was only temporary.

A significant decrease in pH and in concentrations of calcium and phosphorus in the solutions upon boiling is another indication of the formation of apatite (Rathje, 1961). In Table 12, the concentrations of calcium and phosphorus, and the pH all decrease in the solutions after boiling followed by equilibration for 10 hours at 25° C. After a longer time of equilibration (67 days), however, the concentrations of calcium

Table 12. Negative logarithm of ionic concentrations, ionic activities, and lime and phosphate potentials of solutions equilibrated with Florida phosphate rock before and after boiling followed by equilibration at 25° C

Sample no.	Total equilibration times, days	pH	p[Ca]	$p[P]_T$	pF	pCa	pH_2PO_4	pPO_4	$pH_2PO_4 + \frac{1}{2}pCa$	$pH - \frac{1}{2}pCa$
1	77	3.92	1.714	2.065	--	2.07	2.21	13.89	3.24	2.89
	77[a]	3.50	1.747	2.139	4.60	2.09	2.28	14.80	3.33	2.46
	144	3.90	1.710	2.097	4.72	2.06	2.24	13.96	3.27	2.87
2	77	3.90	1.653	2.157	--	2.02	2.31	14.03	3.32	2.89
	77[a]	3.50	1.710	2.305	4.60	2.06	2.46	14.98	3.48	2.47
	144	3.87	1.670	2.270	4.80	2.03	2.42	14.20	3.43	2.86

[a]10 hours after boiling.

Table 13. Values of ($10pCa + 6pPO_4 + 2pF$) and ($pCa + 2pF$) calculated from Table 12

Sample no.	Time after boiling	pH		$10pCa + 6pPO_4 + 2pF$	$pCa + 2pF$
1	10 hours	3.50		119.0	11.29
2	10 hours	3.50		119.6	11.26
			Mean	119.3	11.28
1	67 days	3.90		113.8	11.50
2	67 days	3.87		115.0	11.63
			Mean	114.4	11.57

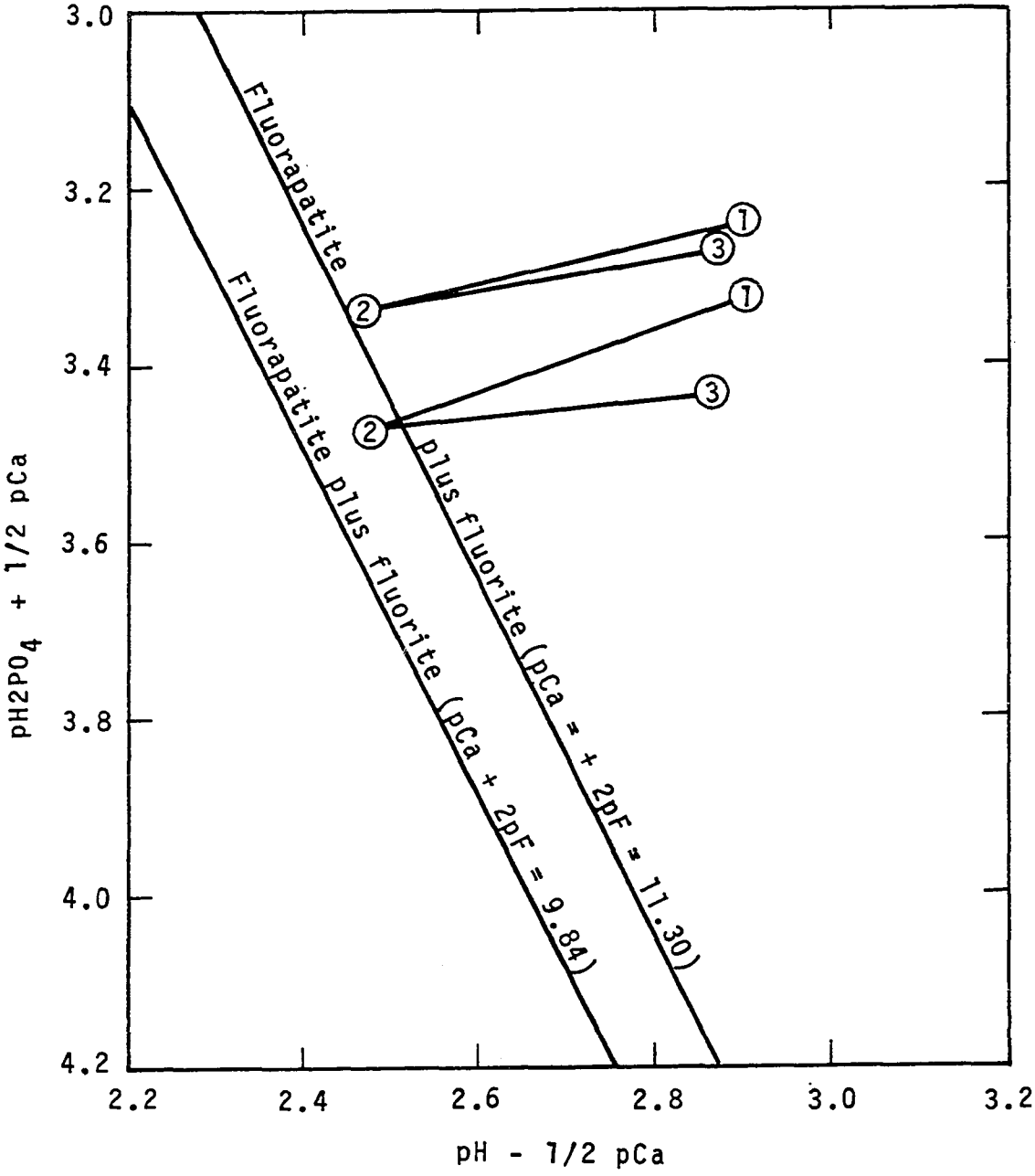

Figure 12. Plot of $pH_2PO_4 + \frac{1}{2}pCa$ versus $pH - \frac{1}{2}pCa$ for solutions equilibrated with Florida phosphate rock. Treatments prior to the analyses indicated by number were as follows: (1) equilibrated 77 days at 25° C, (2) equilibrated 77 days at 25° C, boiled 2 hours, and then equilibrated 10 hours at 25° C, and (3) equilibrated 77 days at 25° C, boiled 2 hours, and then equilibrated 67 more days at 25° C. The line corresponding to pCa + 2pF = 9.84 is saturated with fluorite, but the lines corresponding to pCa + 2pF = 11.3 is unsaturated with fluorite

and phosphorus and the pH all increased toward the values obtained in the solutions before boiling.

There is a possibility that the fluorapatite formed on boiling is on the surface of the carbonate apatite of the phosphate rock. An analogous suggestion was made by Wier et al. (1972) with regard to the transformation of hydroxyapatite to fluorapatite. The following calculations show that the possibility just suggested is not unreasonable. In the case of sample no. 2, the reduced concentration of phosphorus, $\Delta[P]_T$, upon boiling the solution was calculated as

$$\Delta[P]_T = (6.97 - 4.95) \times 10^{-3} = 2.02 \times 10^{-3} \text{ M}$$

the equivalent quantity of fluorapatite formed, $\Delta[FA]$, may be estimated as

$$\Delta[FA] = 2.02 \times 10^{-3}/6 = 3.4 \times 10^{-4} \text{ mole.}$$

The amount of carbonate apatite in phosphate rock dissolved in the solution, $\Delta[CA]$, may be calculated from the chemical formula of carbonate apatite. In this case, the formula was approximated as $Ca_{9.74}Na_{0.21}Mg_{0.05}(PO_4)_{5.19}(CO_3)_{0.81}F_{2.32}$, with a formula weight of 982.2. Thus, 10 g of phosphate rock per 100 ml of solution yielded

$$\Delta[CA] = 6.97 \times 10^{-3} \times \frac{100}{1000} \times \frac{982.2}{5.19} = 0.13 \text{ g of carbonate}$$

apatite in solution.

Since the concentration of carbonate apatite in Florida phosphate rock is approximately 85%, the remaining quantity of solid carbonate apatite may be estimated as 8.50 - 0.13 = 8.37 g. If the surface area of the carbonate apatite is 8 m^2/g (the greatest surface area of synthetic fluorapatite prepared by McCann, 1968), the solid surface area

after the dissolution is approximately 8.37 x 8 = 66.96 m^2 per 100 ml of solution. If the unit cells of fluorapatite are arranged so that their basal plane is exposed to the solution, the surface area of a unit cell may be approximated as $5.2a^2$, where $\underline{a}$ = 9.37 x 10^{-8} cm. Thus, there are approximately

$$\frac{66.96 \times 10^4 \text{ cm}^2}{5.2 \times (9.37 \times 10^{-8})^2 \text{cm}^2} = 1.5 \times 10^{19} \text{ unit cells}$$

exposed to 100 ml of solution. Since a unit cell is a molecule for fluorapatite,

$$\frac{1.5 \times 10^{19}}{6 \times 10^{23}} = 2.5 \times 10^{-5} \text{ mole}$$

of fluorapatite would be needed to form a monolayer on the surface of the carbonate apatite. The calculated quantity of fluorapatite formed was 3.4 x 10^{-4} mole. Therefore, it appears that enough fluorapatite was formed to produce a monolayer on the surface of carbonate apatite upon boiling the solutions equilibrated with Florida phosphate rock.

Experiment 6. Solubility of Florida Phosphate Rock

Introduction

The results from the previous experiments indicated that the equilibration of Florida phosphate rock with solutions at room temperature yielded solutions that were supersaturated with respect to fluorapatite at relatively high pH values and unsaturated with respect to fluorapatite at relatively low pH values. The objective of this experiment was to investigate whether the carbonate apatite in Florida phosphate rock would yield a solubility-product constant at room temperature based on its own chemical formula, $Ca_{9.74}Na_{0.21}Mg_{0.05}(PO_4)_{5.19}(CO_3)_{0.81}F_{2.32}$, rather than

on the formula of fluorapatite, $Ca_{10}(PO_4)_6F_2$.

Procedure

Samples of Florida phosphate rock were equilibrated at 25° C with solutions in the ratios of 1 and 10 g of solid per 100 ml of solution. The initial pH of the solutions was adjusted by addition of dilute HCl. The equilibration period was 30 days. Analyses were made on the solutions for calcium, phosphorus, sodium, magnesium, pH, and pF.

The residues from the first equilibration were equilibrated a second time with addition of distilled water. Approximately one half of the original solution was removed from both sides of the cells before addition of the distilled water. The equilibration period was again 30 days at 25° C before the analyses were made on the solutions.

Results and discussion

The data are given in Table 14. According to the solubility-product principle, a sparingly soluble solid compound equilibrated with solutions should yield a constant ion-activity product (solubility-product constant) at a given temperature when the systems are at equilibrium. The solubility-product constant should be independent of pH and the ratio of solid to solution.

A plot of the negative logarithm of the ion-activity product of the carbonate apatite in the Florida phosphate rock (pI_{CA}) versus the pH of the solutions for the first time of equilibration at 25° C is shown in Figure 13. The results indicate that a constant ion-activity product existed only within a certain range of pH (pH 4.30 to 5.78 with 1 g of solid per 100 ml and pH 4.54 to 6.18 with 10 g of solid per 100 ml). The

Table 14. Negative logarithm of ionic concentrations, ionic activities, and ion-activity products for carbonate apatite when Florida phosphate rock was equilibrated with dilute HCl solutions at 25° C

Grams of solid per 100 ml of solution	Sample no.	pH	p[Ca]	$p[P]_T$	p[Na]	p[Mg]	pF	pI_{CA} [a]
			-First equilibration-					
1	1	2.56	1.492	1.769	3.00	3.38	3.50	126.6
1	2	2.62	1.527	1.803	3.02	3.40	3.50	126.2
1	3	3.14	1.832	2.123	3.33	3.65	3.60	123.6
1	4	3.73	2.098	2.399	3.49	3.87	3.68	119.9
1	5	4.30	2.406	2.674	3.68	4.06	3.75	117.0
1	6	4.33	2.413	2.683	3.66	4.06	3.75	116.7
1	7	4.81	2.694	3.004	3.97	4.16	3.88	115.3
1	8	4.81	2.732	3.029	3.99	4.18	3.92	115.8
1	9	5.08	2.990	3.337	4.13	4.27	4.00	116.6
1	10	5.13	3.016	3.376	4.13	4.29	4.08	116.3
1	11	5.72	3.457	3.878	4.35	4.42	4.22	116.7
1	12	5.74	3.448	3.860	4.31	4.41	4.22	116.2
1	13	5.78	3.476	3.914	4.31	4.42	4.24	116.4
1	14	6.42	3.774	4.343	4.32	4.52	4.22	114.0
10	1	2.21	0.896	1.185	2.43	2.69	3.75	125.2
10	2	2.38	1.014	1.318	2.55	2.76	3.78	124.3
10	3	2.51	1.160	1.436	2.65	2.85	3.88	124.3
10	4	3.25	1.489	1.817	2.98	3.06	3.96	119.2
10	5	4.54	2.165	2.568	3.32	3.32	4.00	112.2
10	6	4.55	2.170	2.572	3.34	2.69	4.00	112.1
10	7	4.94	2.486	2.958	3.47	2.76	4.08	112.1
10	8	4.95	2.483	2.964	3.43	2.85	4.08	112.0
10	9	5.49	2.852	3.494	3.61	3.06	4.06	111.4
10	10	5.54	2.859	3.524	3.57	3.32	4.10	111.1
10	11	5.70	3.059	3.808	3.61	3.38	4.24	112.8
10	12	5.79	3.044	3.800	3.59	3.47	4.16	111.3
10	13	6.13	3.239	4.306	3.61	3.46	4.08	111.6
10	14	6.18	3.234	4.362	3.61	3.59	4.08	111.3
10	15	6.18	3.249	4.353	3.60	3.60	4.08	111.4
			-Second equilibration-					
1	1	3.78	2.302	2.654	3.71	4.20	3.20	121.0
1	2	3.81	2.293	2.639	4.06	4.19	3.25	120.8
1	3	4.26	2.482	2.923	4.25	4.44	3.23	118.0

[a] $pI_{CA} = 9.74pCa + 0.21pNa + 0.05pMg + 5.19pPO_4 + 0.81pCO_3 + 2.32pF.$

Table 14. (Continued)

Grams of solid per 100 ml of solution	Sample no.	pH	p[Ca]	$p[P]_T$	p[Na]	p[Mg]	pF	pI_{CA} [a]
1	4	4.62	2.804	3.242	4.32	4.71	3.28	118.1
1	5	5.05	3.141	3.500	4.47	4.88	3.70	118.6
1	6	5.06	3.095	3.481	4.48	4.88	3.70	118.0
1	7	5.41	3.413	3.711	4.65	5.05	3.84	118.3
1	8	5.41	3.380	3.702	4.60	5.02	3.92	118.1
1	9	5.53	3.451	3.778	4.64	4.98	3.92	117.7
1	10	5.54	3.451	3.778	4.66	4.95	4.00	117.8
1	11	5.71	3.524	3.912	4.65	4.88	4.32	117.9
1	12	5.72	3.482	3.843	4.59	4.84	4.32	117.0
1	13	5.70	3.524	3.897	4.62	4.88	4.32	118.1
1	14	5.92	3.603	3.988	4.55	4.84	4.58	117.2
10	1	3.34	1.652	1.964	3.13	3.39	3.42	118.6
10	2	3.55	1.758	2.087	3.24	3.49	3.60	117.8
10	3	3.73	1.887	2.210	3.34	3.60	3.65	117.3
10	4	4.26	2.249	2.560	3.64	3.86	3.70	115.5
10	5	5.29	2.871	3.242	4.01	4.07	3.75	111.8
10	6	5.25	2.851	3.235	4.00	4.05	3.75	112.2
10	7	5.61	3.051	3.516	4.05	4.05	4.07	112.0
10	8	5.63	3.035	3.485	4.03	4.03	4.07	111.4
10	9	6.02	3.210	3.948	4.09	4.03	4.40	111.6
10	10	6.04	3.191	3.957	4.10	4.03	4.40	111.3
10	11	6.11	3.258	4.111	4.11	4.01	4.45	112.0
10	12	6.16	3.263	4.131	4.09	4.01	4.50	111.0
10	13	6.25	3.302	4.286	4.06	3.98	4.55	111.8
10	14	6.28	3.302	4.308	4.08	3.97	4.55	111.7
10	15	6.29	3.302	4.312	4.04	3.97	4.60	111.5

average values of pI_{CA} for the two systems within the pH ranges mentioned were 116.3 and 111.8 with 1 and 10 g of solid per 100 ml of solution. The existence of two different constant ion-activity products, depending on the ratio of solid to solution, is not in accord with the solubility-product principle.

The solubility behavior of the apatite of phosphate rock in this

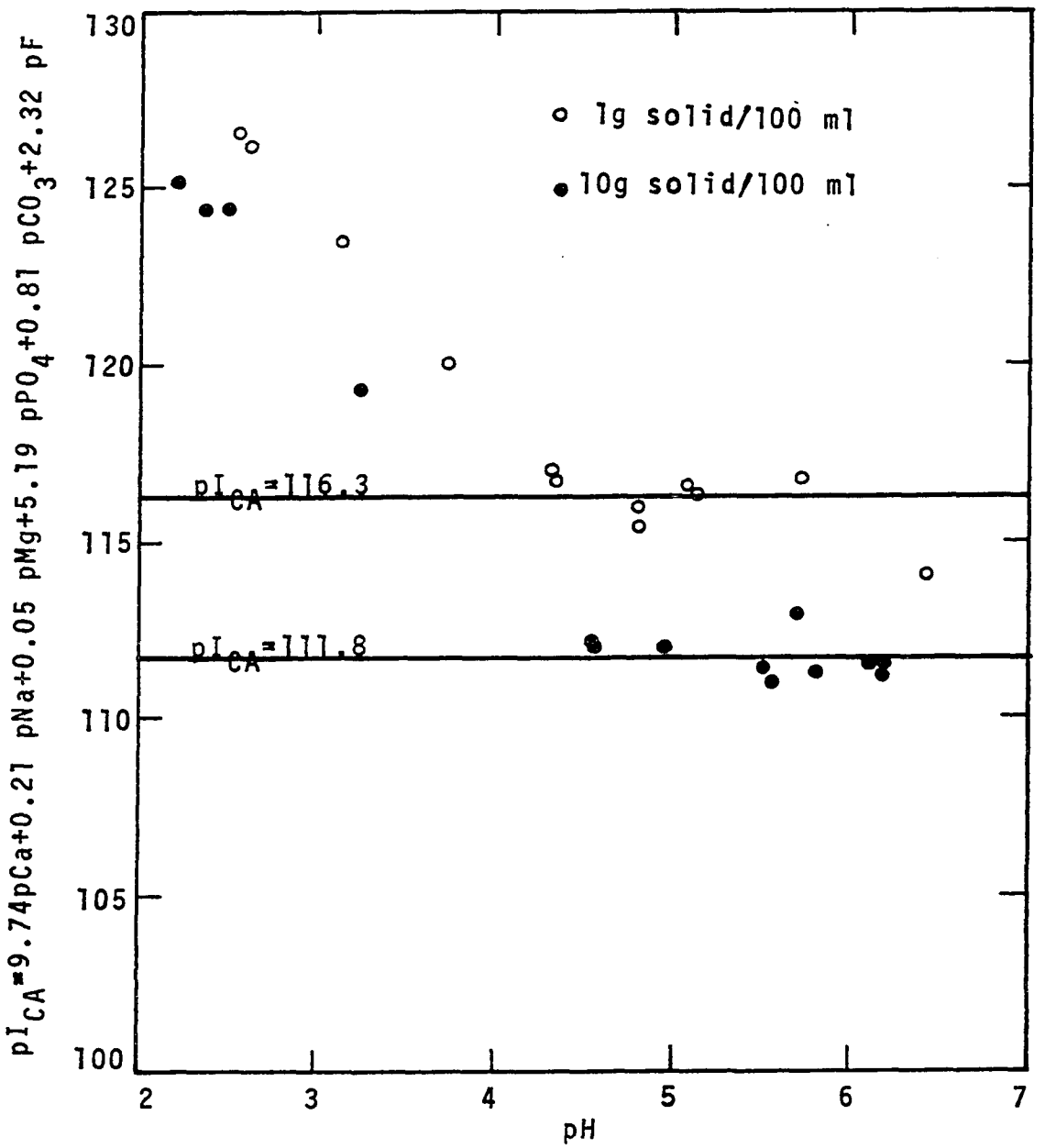

Figure 13. Negative logarithm of ion-activity product of carbonate apatite in Florida phosphate rock versus pH in solutions obtained in the first equilibration with two different ratios of solid to solution

experiment is analogous to that observed with synthetic hydroxyapatite by Wier (1968) and by the author in work reported earlier in this thesis. To account for the behavior, Wier (1968) proposed the "activity" concept, according to which the apatite in a given sample may have various activities or stabilities, each of which corresponds to a different solubility or ion-activity-product constant. The portion of the sample with the highest activity or solubility dissolves preferentially. As more and more of the solid is dissolved, the activity of the residual solid with which the solution is in equilibrium becomes lower and lower, and the solubility similarly becomes lower and lower. Hence, the solubility value obtained with a low ratio of solid to solution is lower than that obtained with a higher ratio of solid to solution because a greater proportion of the solid dissolves in the former case than in the latter. At high pH values, where little of the solid dissolves, the solubility value obtained with a low ratio of solid to solution approaches that obtained with a higher ratio of solid to solution.

The observation by Lehr et al. (1967) that the apatite in almost all sedimentary phosphate rocks is poorly crystallized provides some reason to suppose that the explanation developed for synthetic hydroxyapatite may apply also to the carbonate apatite in Florida phosphate rock. In solubility experiments with another naturally occurring mineral, kaolinite, Kittrick (1966) found that the ion-activity-product constant decreased as a result of successive extractions of the samples with dilute HCl solution prior to the solubility measurements. The X-ray pattern was not changed by the preliminary extractions. Thus, he concluded that "a minor amount of more soluble component might not be detected by X-ray diffraction, yet

if it occurred as small particles, its solubility characteristics could dominate the system."

Verification of the applicability of Wier's (1968) activity concept to the carbonate apatite in Florida phosphate rock may be found in Figure 14, which contains plots of $[P]_T$ against pH. The points obtained with 1 g of solid per 100 ml lie above those obtained with 10 g of solid per 100 ml at low pH values, indicating lower solubility of carbonate apatite in the former case than in the latter. As the pH increased, the plots representing the two ratios of solid to solution converged.

Figure 15 shows a plot of pI_{CA} versus pH of solutions equilibrated for the second time with Florida phosphate rock at 25° C for 30 days. Again, an ion-activity-product constant existed only within a certain range of pH of the equilibrated solutions. In Table 14 the average pI_{CA} values for the systems with 1 g of solid per 100 ml ($pH \geqslant 4.26$) and 10 g of solid per 100 ml ($pH \geqslant 5.29$) were 117.9 and 111.8, respectively. The value obtained with 10 g per 100 ml was the same as for the first equilibration ($pI_{CA} = 111.8$). With 1 g of solid per 100 ml, however, the value of pI_{CA} increased from 116.3 in the first equilibration to 117.9 in the second. This observation clearly indicates a decrease in solubility of the solid carbonate apatite that was in contact with the solution in the second equilibration.

As can be seen from Figure 16, the phosphorus concentrations obtained in the second equilibration were lower than those in the first equilibration at low pH values. As the pH increased, however, the trends of points representing the first and second equilibrations converged. Figure 17 shows a plot of $p[P]_T$ against pH for the first and second equilibrations

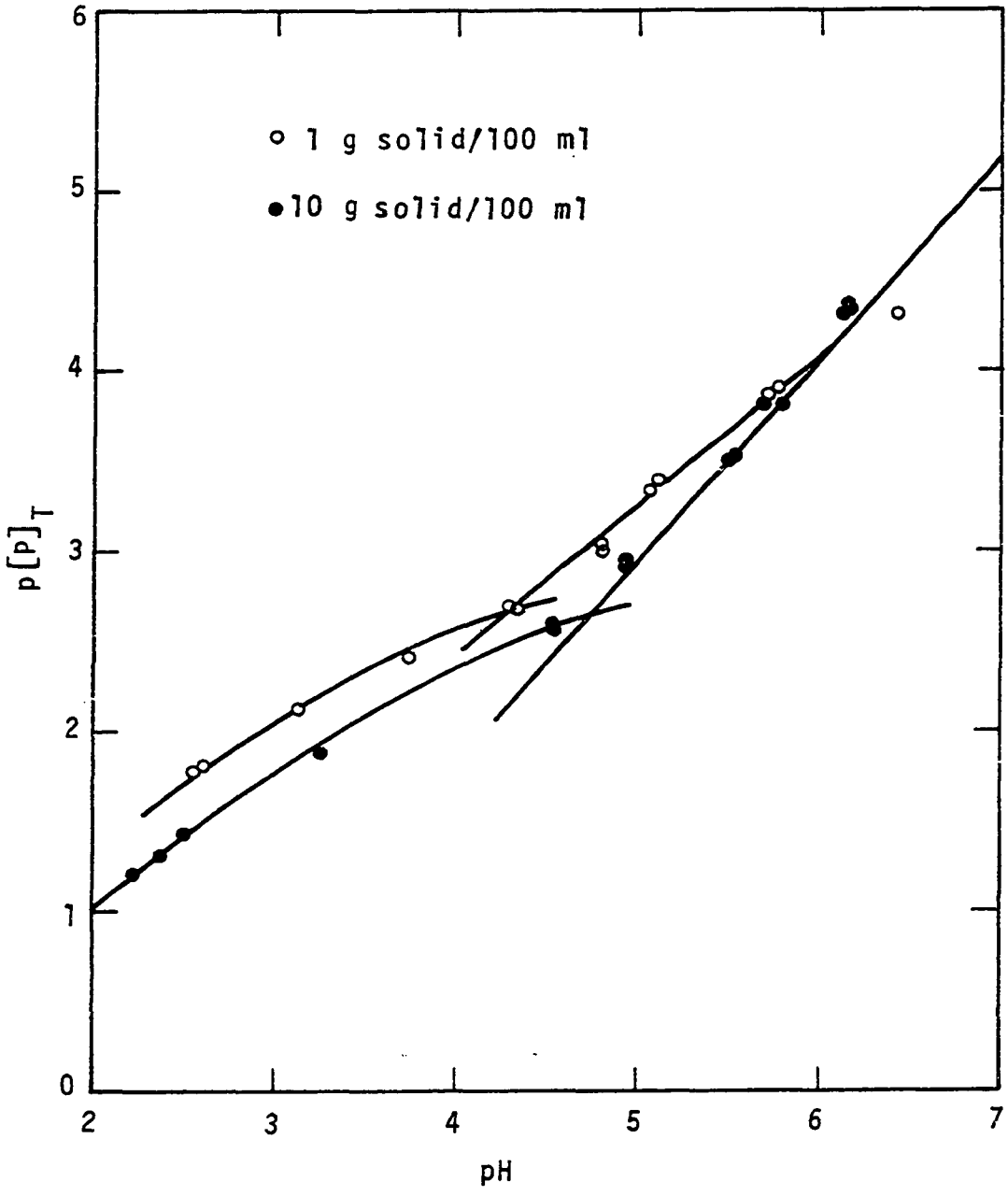

Figure 14. Negative logarithm of phosphorus concentration versus pH as found in the first equilibration of Florida phosphate rock with dilute hydrochloric acid solutions at two different ratios of solid to solution

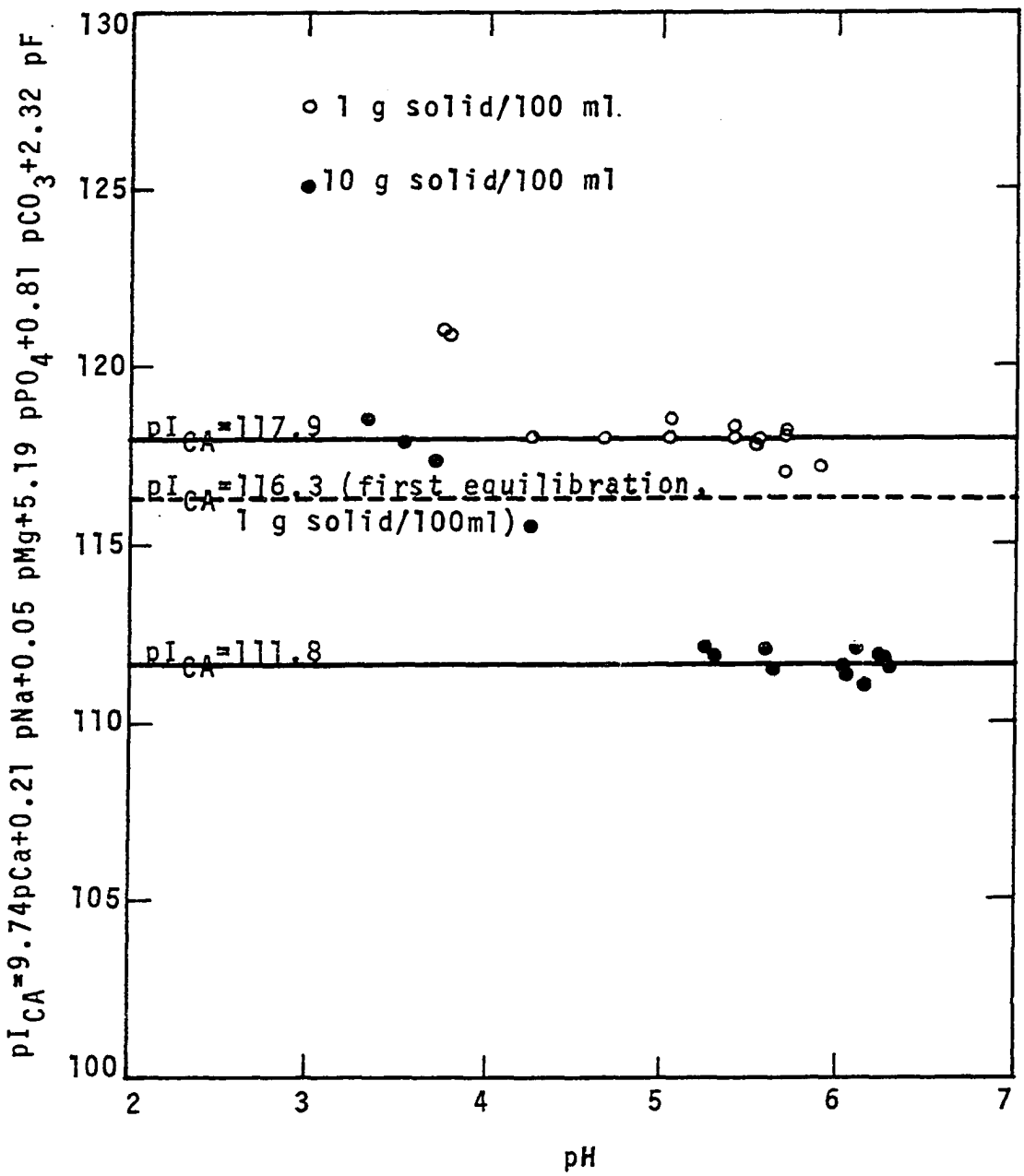

Figure 15. Negative logarithm of ion-activity product of carbonate apatite in Florida phosphate rock versus pH in solutions obtained in the second equilibration with two different ratios of solid to solution

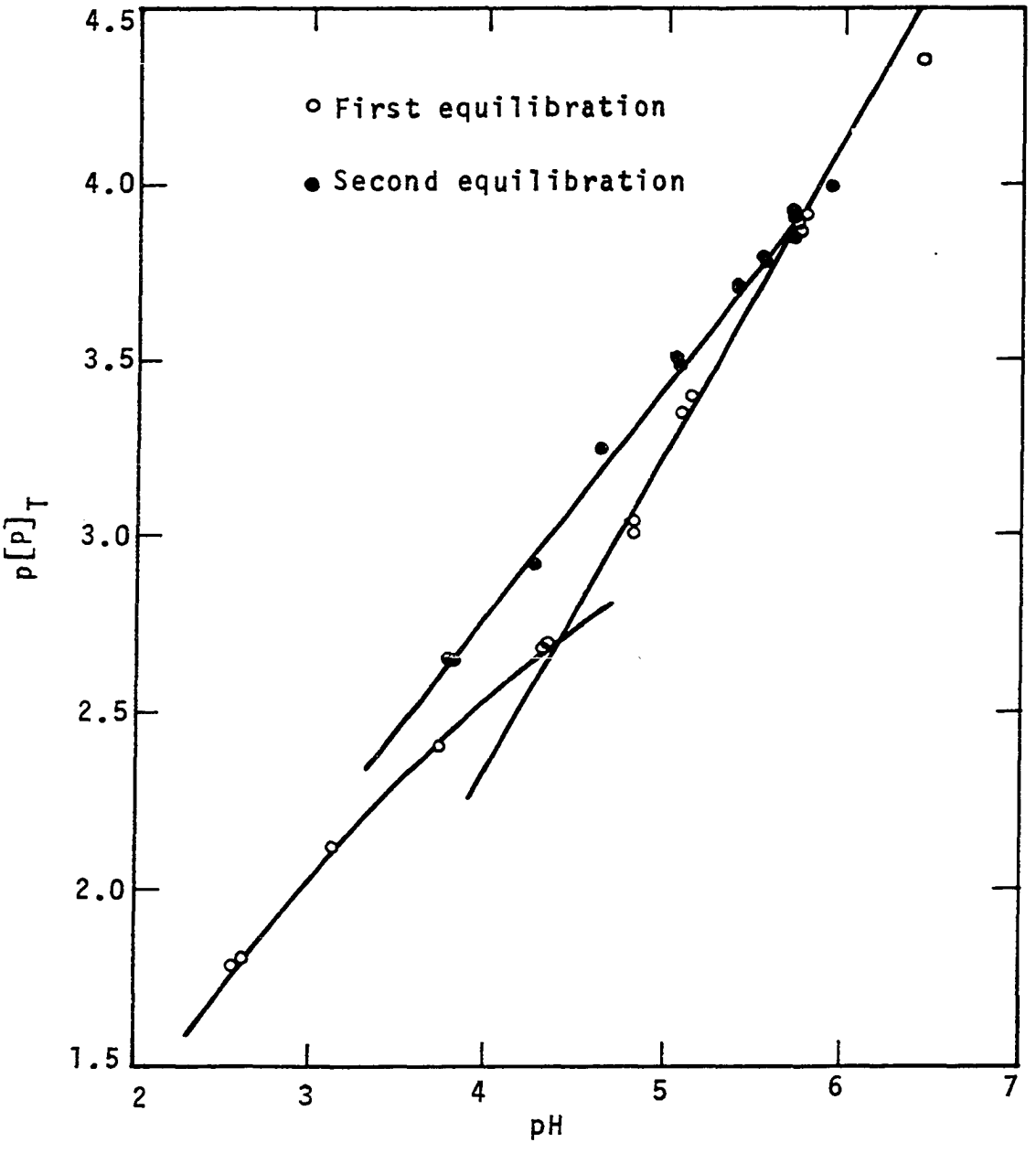

Figure 16. Negative logarithm of phosphorus concentration versus pH as found in the first and second equilibrations of Florida phosphate rock with solutions in the quantity of 1 g of solid per 100 ml of solution

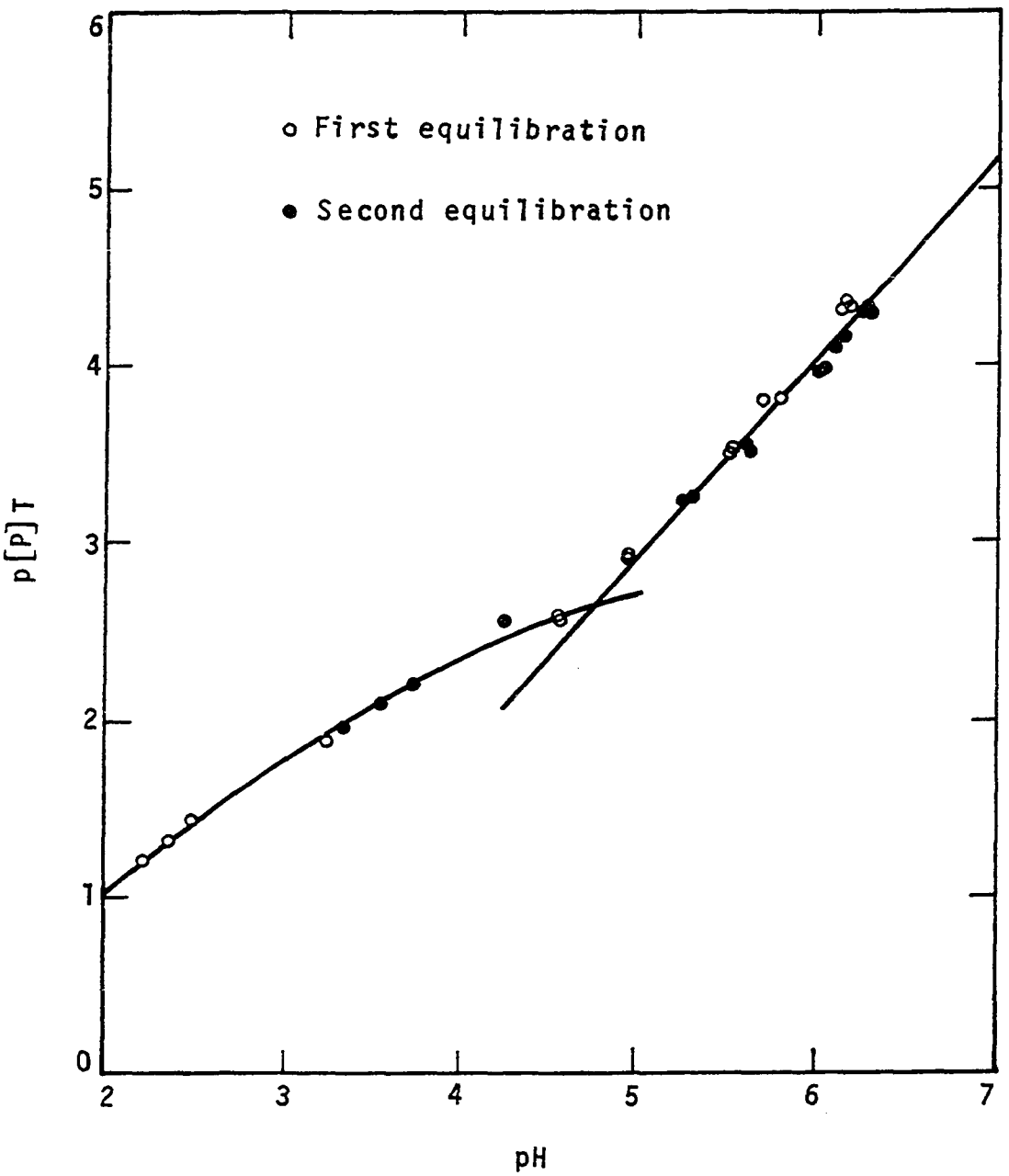

Figure 17. Negative logarithm of phosphorus concentration versus pH as found in the first and second equilibrations of Florida phosphate rock with solutions in the quantity of 10 g of solid per 100 ml of solution

in the system containing 10 g of solid per 100 ml. The trend of phosphorus concentrations with pH appeared to be the same in the first and second equilibrations. These observations all verify Wier's (1968) activity concept.

Experiment 7. Solubility of Citrate-Extracted Florida Phosphate Rock

Introduction

Examination of the sample of Florida phosphate rock by the methods of X-ray diffraction, infrared absorption, and optical mineralogy failed to demonstrate the presence of alkaline-earth carbonates. Nevertheless, the possibility exists that the solubility behavior of the carbonate apatite might be modified by the presence of quantities of alkaline-earth carbonates too small to be detected by the methods mentioned.

The objective of this experiment was to determine the ion-activity product of carbonate apatite in Florida phosphate rock which had been extracted several times with an alkaline ammonium citrate solution that dissolves alkaline-earth carbonates but removes only a small quantity of carbonate apatite. It was considered that the ion-activity product of the citrate-extracted material should be uninfluenced by alkaline-earth carbonates.

Procedure

One hundred grams of Florida phosphate rock were placed in a liter of alkaline ammonium citrate solution. The phosphate rock was digested at 65° C for 4 hours with frequent agitation, after which the mixture

was allowed to stand at room temperature for 18 hours. The mixture was filtered, fresh citrate solution was added, and the phosphate rock was digested again. The digestion was repeated for two more times. Finally the residue was washed with distilled water and dried at 105° C.

According to Silverman et al. (1952), the solubility of calcite in the citrate solution is 0.66 g per 100 ml of solution. Accordingly, the maximum amount of calcite dissolved after four treatments should be approximately 26.4 g, an amount equivalent to 26.4% of the weight of the 100-g sample of Florida phosphate rock. Because the identification methods used should have been capable of detecting as little as 1% alkaline-earth carbonate in the phosphate rock, it is reasonable to assume that alkaline-earth carbonates were absent from the citrate-extracted Florida phosphate rock.

The ratio of solid to solution was 1 g per 100 ml, and two successive equilibrations were made, both for 30 days at 25° C. The solutions used were less acid in the second equilibration than in the first.

Results and discussion

The results are given in Table 15. The values of pI_F, pI_{FA}, and pI_{CA} were all calculated to investigate the nature of the solid phase or phases in equilibrium with the solutions.

Figure 18 shows a plot of $p[P]_T$ versus p[Ca] together with the theoretical line. The theoretical line represents the results that would be obtained if the ratio of the concentration of total phosphorus to calcium in the equilibrated solutions were the same as the ratio in the portion of the solid dissolved by warm, 3N HCl (presumably the apatite

Table 15. Negative logarithm of ionic concentrations, ionic activities, and ion-activity products for fluorite, fluorapatite, and carbonate apatite when citrate-extracted Florida phosphate rock was equilibrated with dilute HCl solutions

Sample no.	pH	p[Ca]	$p[P]_T$	pNa	pMg	pF	pI_F [a]	pI_{FA} [b]	pI_{CA} [c]
				-First equilibration-					
1	2.48	1.421	1.629	3.09	4.02	3.55	8.96	124.6	126.3
2	2.87	1.679	1.950	3.32	4.06	3.50	9.04	123.0	124.5
3	3.16	1.825	2.124	3.45	4.13	3.60	9.35	121.5	123.0
4	3.81	2.150	2.382	3.65	4.29	3.67	9.74	117.6	118.9
5	4.23	2.367	2.637	3.91	4.51	3.72	10.02	115.8	117.0
6	4.54	2.603	2.918	4.13	4.66	3.84	10.46	116.0	116.9
7	4.86	2.864	3.282	4.39	4.82	4.05	11.11	117.0	117.7
8	5.57	3.427	3.842	4.73	5.07	4.32	12.18	117.7	118.0
				-Second equilibration-					
1	4.34	2.767	3.067	4.26	4.85	3.28	9.49	119.6	120.7
2	4.47	2.891	3.227	4.33	4.94	3.28	9.60	120.0	121.0
3	4.68	2.982	3.327	4.38	4.98	3.42	9.96	119.2	120.2
4	4.95	3.232	3.542	4.63	5.20	3.51	10.38	119.8	120.6
5	5.11	3.353	3.647	4.74	5.34	3.70	10.87	120.0	120.8
6	6.32	3.952	4.361	5.12	5.82	3.70	11.46	116.0	116.0
8	6.56	4.183	4.617	5.10	5.80	4.05	12.40	117.9	117.4

[a] $pI_F = pCa + 2pF$.

[b] $pI_{FA} = 10pCa + 6pPO_4 + 2pF$.

[c] $pI_{CA} = 9.74pCa + 0.22pNa + 0.04pMg + 5.19pPO_4 + 0.81pCO_3 + 2.32pF$.

fraction). The number of moles of phosphorus and calcium per mole of carbonate apatite were 5.19 and 9.74, respectively. Therefore, stoichiometric dissolution of carbonate apatite should yield,

$$[P]_T/[Ca] = 5.19/9.74.$$

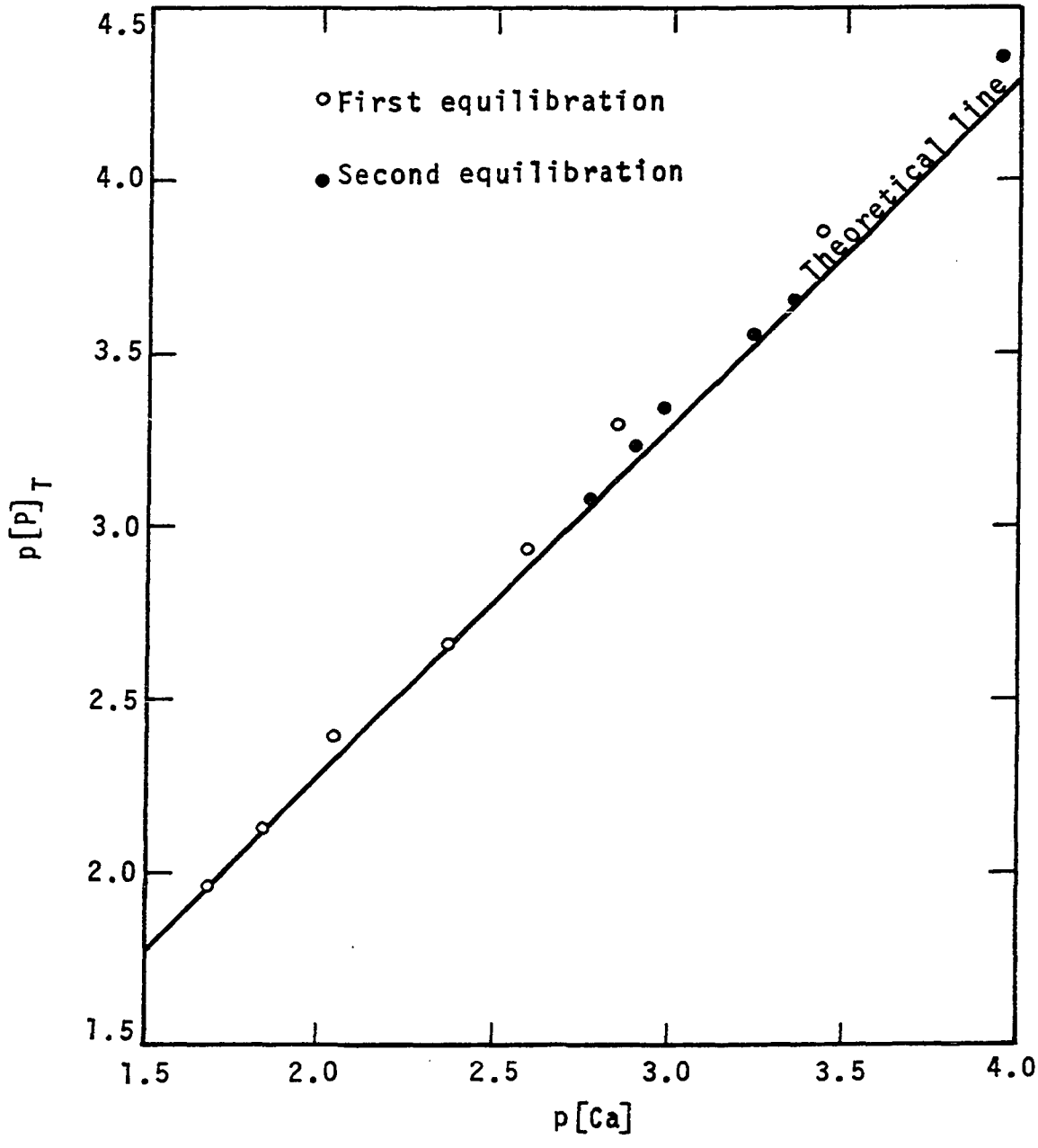

Figure 18. Negative logarithm of phosphorus concentration versus negative logarithm of calcium concentration in solutions equilibrated with citrate-extracted Florida phosphate rock

Taking the negative logarithm,

$$p[P]_T = 0.27 + p[Ca]. \quad (37)$$

According to equation 37, a plot of $p[P]_T$ versus p[Ca] should yield a straight line with a slope of 1 and an intercept of 0.27. Figure 18 shows that the points of the observed data for $p[P]_T$ and p[Ca] were fairly close to the theoretical line, which indicates that the dissolution of the carbonate apatite was substantially stoichiometric and that, if other components that yielded calcium and phosphorus to the solution were present, they were either present in small amounts or they released calcium and phosphorus in the same ratio as the apatite component.

Figure 19 shows a plot of pI_{CA} against pH of the solutions. The average values of pI_{CA} within the pH range of 4 to 6 were 117.7 and 120.7 for the first and the second equilibrations, respectively. The value of 117.7 is very close to the value of 117.9 obtained by equilibrating unextracted Florida phosphate rock for the second time (Figure 15), but it is greater than the value of 116.3 obtained for the first equilibration of the unextracted rock. The significant increase of pI_{CA} from the first equilibration to the second in this experiment is inferred to be a consequence of a decrease in the activity of the residual solid carbonate apatite from the first equilibration to the second.

Chaverri and Black (1966) found that, with successive extractions of phosphate rock with dilute HCl, the solubility behavior approached that for solutions in equilibrium with solid fluorapatite and fluorite. Since the activity of fluorapatite is lower than that of carbonate apatite (Lehr et al., 1967), it is of interest to determine whether the surface of the citrate-extracted Florida phosphate rock quilibrated for the second time

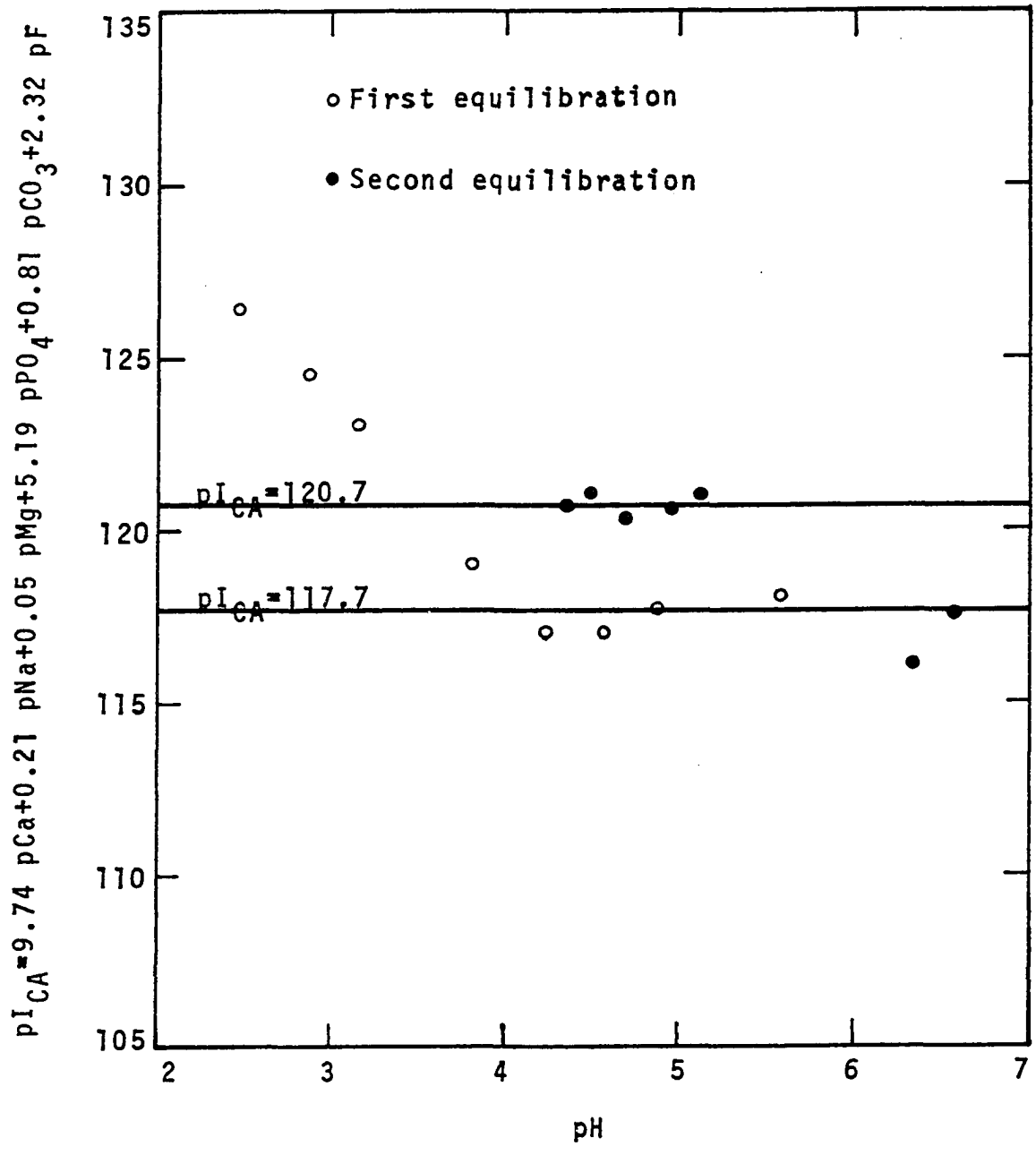

Figure 19. Negative logarithm of ion-activity product of carbonate apatite versus pH in solutions obtained in two successive equilibrations of citrate-extracted Florida phosphate rock with dilute hydrochloric acid

(pI_{CA} = 120.7) is in the form of newly formed fluorapatite or in the form of carbonate apatite with very low activity. Figure 20 shows a plot of pI_{FA} against pH of the equilibrated solutions. The average value of pI_{FA} for the second equilibration within the pH range of 4 to 6 is 119.7. It compares favorably with the value 118.4 for pure fluorapatite calculated by Lindsay and Moreno (1960) from thermodynamic data, the value 118.8 obtained by Wier et al. (1972) in work on the transformation of hydroxyapatite to fluorapatite, the value 119.2 obtained by McCann (1968) in work with dilute solutions, and the value 120.9 obtained by Farr and Elmore (1962) in work on solutions with high ionic strength and low pH values. The results are thus consistent with the view that, in the second equilibration of Florida phosphate rock with dilute HCl, the solutions in the pH range of 4 to 6 were in equilibrium with newly formed fluorapatite. The average value of pI_{FA} for the first equilibration is 116.8. In the first equilibration, therefore, the solutions were supersaturated with respect to fluorapatite.

Experiment 8. Solubility of Acid-Extracted Florida Phosphate Rock

Introduction

The results obtained in the preceding experiment show that the solutions equilibrated with the citrate-extracted Florida phosphate rock for the second time at 25° C yielded a pI_{CA} value of 120.7. The corresponding value for pI_{FA} was 119.7 which is close to the value of pure fluorapatite (pK_{FA} = 119.2 according to McCann, 1968).

The objectives of this experiment were (1) to determine the ion-

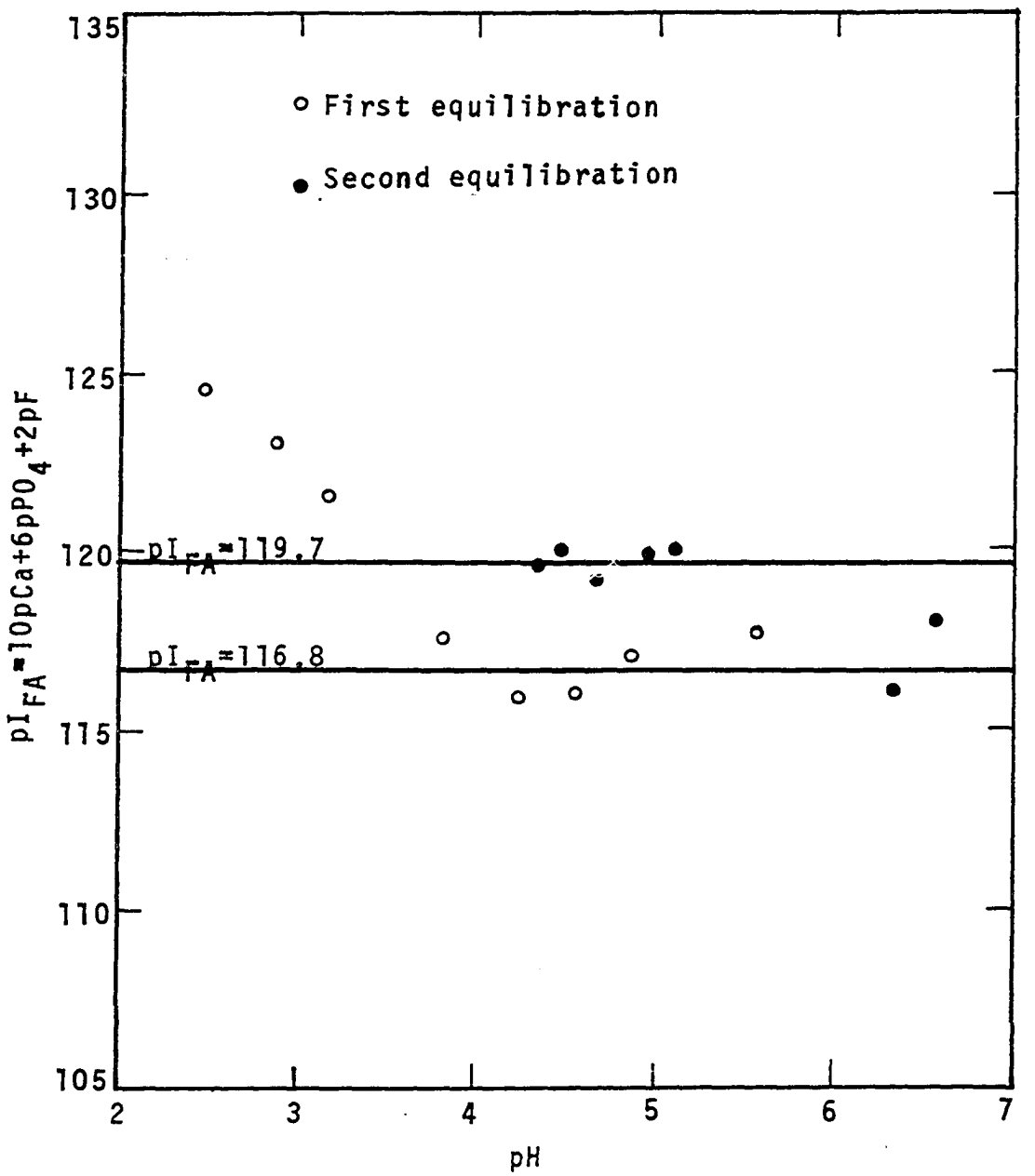

Figure 20. Negative logarithm of ion-activity product of fluorapatite versus pH in solutions obtained in two successive equilibrations of citrate-extracted Florida phosphate rock with dilute hydrochloric acid

activity product of carbonate apatite in Florida phosphate rock that had been extracted several times with dilute HCl solution, (2) to investigate whether the solutions were saturated with carbonate apatite of low activity or with newly formed fluorapatite, and (3) to determine whether there is a minimum ion-activity product for carbonate apatite in Florida phosphate rock.

Procedure

Three 200-g samples of Florida phosphate rock were extracted with 0.3N HCl on a hot plate. The solutions were boiled for several hours, followed by filtration. Two of the three samples were treated in the same way several more times. The three samples will be called "7%-extracted," "16%-extracted," and "27%-extracted" phosphate rocks according to the percentage of the weight of the phosphate rock that has been extracted. All the samples were washed with distilled water and dried at 110° C prior to solubility measurements.

The solubility measurements were made in the same way as in previous experiments. Two ratios of solid to solution were used, 1 and 10 g per 100 ml. The original unextracted Florida phosphate rock was also used to determine the effect of extraction with acid on the solubility.

Results and discussion

The results are given in Table 16. Again, a relatively constant pI_{CA} value was obtained within a certain range of pH of the solution. The averages of the pI_{CA} values in the pH range in which the pI_{CA} values were relatively constant are given in Table 17. For the unextracted Florida phosphate rock, the average pI_{CA} values were 116.6 and 110.8 in

Table 16. Negative logarithm of ionic concentrations, ionic activities, and ion-activity products for carbonate apatite and fluorapatite when unextracted and acid-extracted samples of Florida phosphate rock were equilibrated with dilute HCl solutions at 25° C

Grams of solid per 100 ml of solution	pH	p[Ca]	$p[P]_T$	p[Na]	p[Mg]	pF	pI_{CA} [a]	pI_{FA} [b]
			-Unextracted phosphate rock-					
1	3.24	1.840	2.156	3.39	3.69	3.48	122.3	120.6
1	4.02	2.137	2.459	3.63	3.95	3.63	116.9	115.3
1	4.04	2.156	2.462	3.69	3.97	3.65	116.8	115.2
1	4.85	2.825	3.160	4.15	4.30	3.73	116.4	115.0
1	5.45	3.071	3.444	4.26	4.36	3.90	116.3	112.6
1	5.76	3.313	3.748	4.07	4.40	3.90	116.4	113.0
10	3.65	1.586	1.943	3.02	3.17	4.00	115.7	113.6
10	4.30	1.852	2.240	3.17	3.30	4.14	111.4	109.7
10	4.78	2.205	2.674	3.33	3.41	4.00	110.1	108.8
10	4.81	2.210	2.687	3.33	3.42	4.00	109.9	108.5
10	5.24	2.603	3.261	3.63	3.64	4.02	110.9	110.0
10	5.58	2.876	3.742	3.56	3.58	4.00	111.6	111.2
10	6.19	3.162	4.543	3.63	3.68	3.82	110.8	111.2
			-7%-extracted phosphate rock-					
1	3.10	1.847	2.185	3.55	3.75	3.48	124.2	122.5
1	3.70	2.175	2.481	3.65	4.07	3.82	121.0	120.0
1	3.72	2.175	2.500	3.69	4.12	3.80	121.4	119.8
1	4.80	3.077	3.439	4.43	4.97	3.63	120.5	119.2
1	4.96	3.268	3.653	4.60	5.09	3.57	121.4	120.8
1	5.15	3.378	3.734	4.55	5.06	3.65	120.3	119.8
10	3.25	1.558	1.903	3.11	3.39	4.00	120.2	118.1
10	3.60	1.846	2.179	3.35	3.67	4.00	119.2	117.4
10	4.01	2.127	2.489	3.61	3.96	3.96	119.8	118.9
10	4.54	2.734	3.029	4.04	4.36	4.00	119.4	118.2
10	4.72	3.083	3.305	4.18	4.58	3.85	120.9	120.0
10	4.78	3.164	3.305	4.20	4.63	3.52	119.7	118.8

[a] $pI_{CA} = 9.74pCa + 0.21pNa + 0.05pMg + 5.19pPO_4 + 0.81pCO_3 + 2.32pF.$

[b] $pI_{FA} = 10pCa + 6pPO_4 + 2pF.$

Table 16. (Continued)

Grams of solid per 100 ml of solution	pH	p[Ca]	$p[P]_T$	p[Na]	p[Mg]	pF	pI_{CA} [a]	pI_{FA} [b]
			-16%-extracted phosphate rock-					
1	3.00	1.855	2.188	3.37	3.79	3.48	125.4	123.7
1	3.49	2.156	2.436	3.66	4.14	3.30	122.5	121.0
1	3.52	2.156	2.455	3.64	4.10	3.48	122.7	121.2
1	4.13	2.489	2.803	3.97	4.48	3.48	119.8	118.5
1	4.41	2.722	3.017	4.17	4.68	3.34	119.2	118.4
1	4.71	3.105	3.565	4.43	5.04	3.65	121.6	120.9
1	4.87	3.205	3.690	4.57	5.15	3.57	121.4	120.8
1	5.02	3.427	3.722	4.66	5.24	3.48	121.4	119.8
10	3.00	1.565	1.873	3.14	3.43	3.52	122.0	120.2
10	3.35	1.832	2.140	3.38	3.71	3.65	121.2	119.4
10	3.73	2.141	2.427	3.65	4.01	3.65	120.3	119.3
10	3.72	2.141	2.445	3.65	4.02	3.82	120.9	119.3
10	4.12	2.465	2.730	3.93	4.30	3.63	119.7	118.3
10	4.22	2.694	2.902	4.07	4.43	3.45	120.9	119.9
10	4.47	2.969	3.091	4.23	4.65	3.57	121.5	120.5
10	4.52	3.001	3.124	4.24	4.69	3.40	121.0	120.1
			-27%-extracted phosphate rock-					
1	3.05	1.843	2.157	3.36	3.85	3.14	123.9	122.3
1	3.47	2.141	2.454	3.63	4.14	3.12	122.4	121.0
1	3.48	2.156	2.465	3.64	4.14	3.28	122.8	121.3
1	4.04	2.473	2.779	4.01	4.61	3.22	120.0	118.8
1	4.40	2.728	3.040	4.16	4.73	3.30	119.4	118.4
1	4.72	3.059	3.365	4.47	5.05	3.30	119.5	118.8
1	4.98	3.205	3.518	4.58	5.16	3.70	119.7	118.9
1	5.02	3.261	3.577	4.55	5.09	3.70	119.5	119.0
10	2.93	1.569	1.866	3.17	3.52	3.48	122.8	120.9
10	3.28	1.825	2.103	3.41	3.80	3.48	121.4	119.7
10	3.67	2.138	2.408	3.67	4.09	3.40	120.3	118.8
10	3.67	2.138	2.408	3.69	4.08	3.30	120.1	118.6
10	4.04	2.457	2.696	3.94	4.34	3.28	119.6	118.3
10	4.20	2.649	2.858	4.04	4.48	3.14	119.8	118.7
10	4.40	2.879	3.054	4.18	4.59	3.28	120.2	119.3
10	4.50	2.904	3.090	4.19	4.58	3.14	119.6	118.7

Table 17. Average values of pI_{CA} and pI_{FA} for the unextracted and acid-extracted Florida phosphate rocks at 25° C

Proportion of rock extracted, %	Grams of solid per 100 ml of solution	pI_{CA}	pI_{FA}
0	1	116.6	114.2
	10	110.8	109.9
7	1	120.8	119.5
	10	120.0	118.5
16	1	120.7	119.7
	10	120.8	119.5
27	1	119.6	118.8
	10	120.0	118.7

the systems with 1 and 10 g of solid per 100 ml, respectively. These values are in good agreement with the corresponding values obtained in Experiment 6 (116.3 and 111.8)

Although the pI_{CA} values shown in Table 17 were affected by the ratio of solid to solution in the case of the unextracted phosphate rock, they were independent of the ratio of solid to solution with the acid-extracted samples. The pI_{CA} values of the acid-extracted samples seem to be essentially unaffected by the percentage of phosphate rock that was extracted before the solubility tests. The overall picture may be seen in Figure 21 and 22. The value of pI_{CA} = 120.3 shown in these figures was obtained by averaging all the pI_{CA} values in the constant range for the acid-extracted Florida phosphate rocks in Table 16. This value compares with 120.7 obtained in the second equilibration of citrate-extracted Florida phosphate rock with dilute HCl solutions in experiment 7.

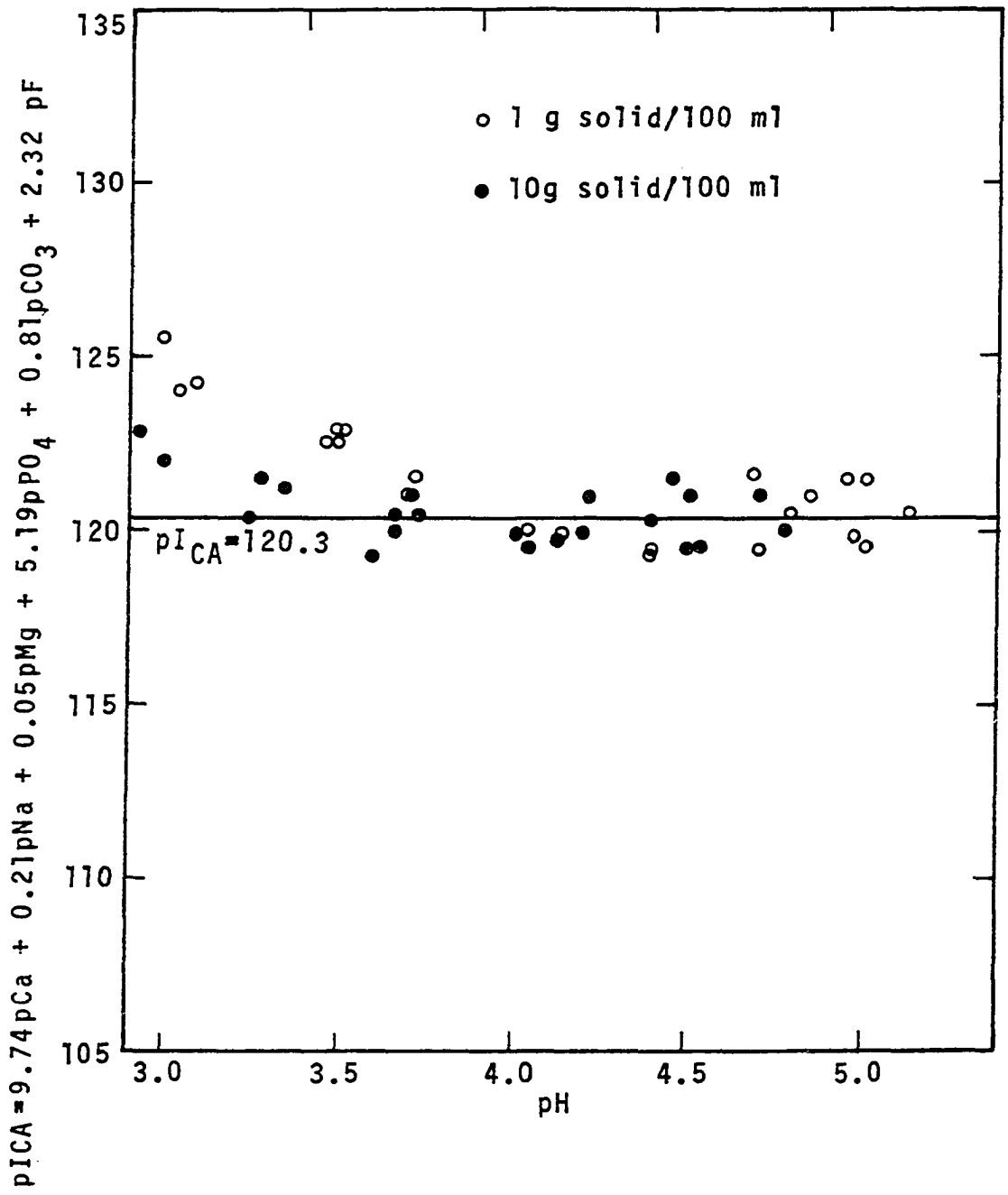

Figure 21. Negative logarithm of ion-activity product of carbonate apatite versus pH in solutions obtained in equilibration of acid-extracted Florida phosphate rock with dilute hydrochloric acid in quantities of 1 and 10 g of phosphate rock per 100 ml of solution

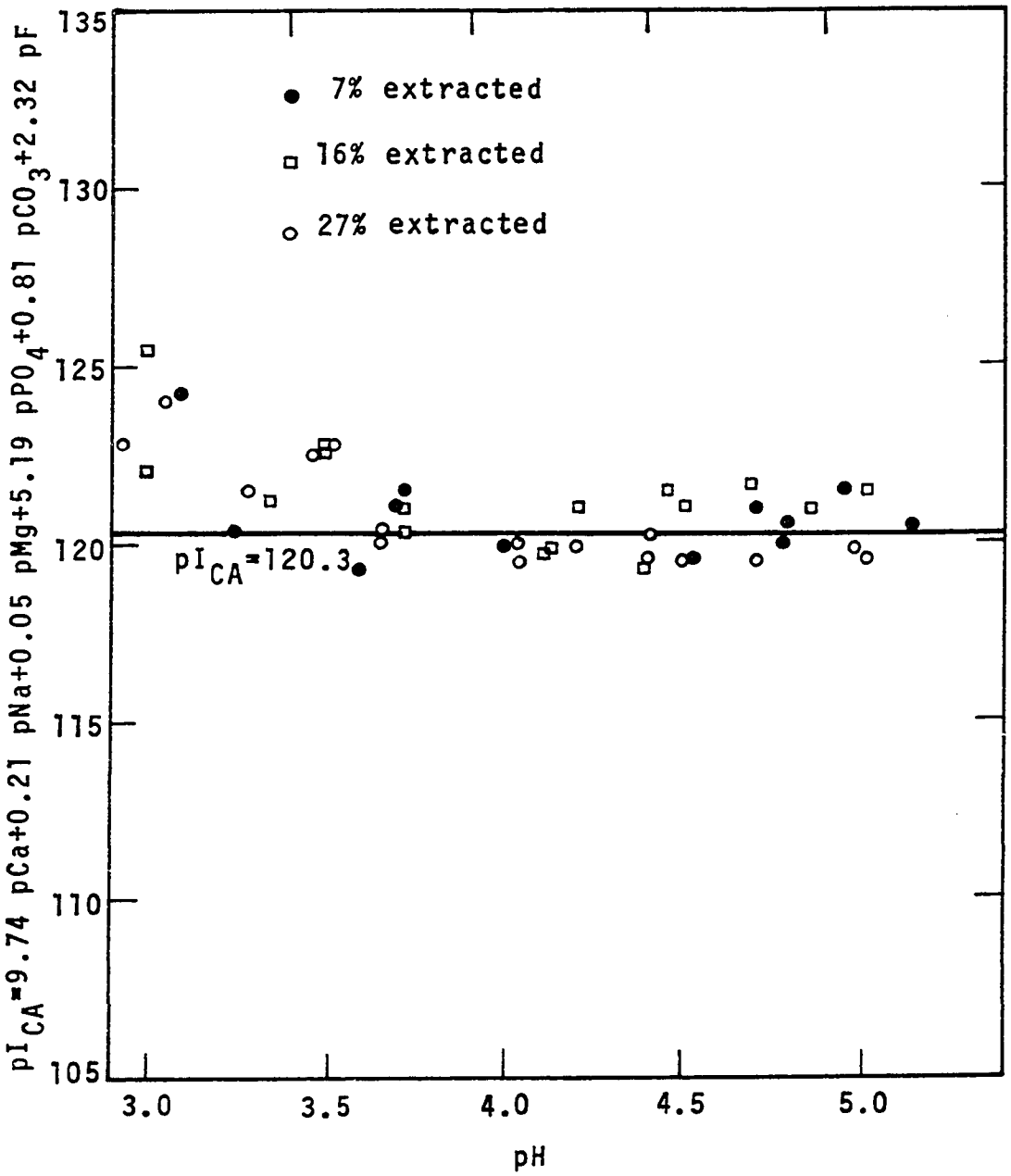

Figure 22. Negative logarithm of ion-activity product of carbonate apatite versus pH in solutions obtained in equilibrations of acid-extracted Florida phosphate with dilute hydrochloric acid. The samples of phosphate rock had previously been extracted with hydrochloric acid to remove 7, 16, or 27% of the weight of the rock

The results show that the negative logarithm of the ion-activity product for carbonate apatite in acid-extracted phosphate rock was higher than that for carbonate apatite in unextracted phosphate rock. Furthermore, negative logarithm of the ion-activity product for carbonate apatite (Table 17) remained essentially the same in all acid-extracted samples irrespective of the proportion of the phosphate rock extracted. These findings suggest that the highest value of the negative logarithm of the solubility-product constant (corresponding to the lowest solubility) for the carbonate apatite in Florida phosphate rock is in the range from 120.3 to 120.7.

In connection with experiment 7, it was suggested that fluorapatite may have formed when citrate-extracted Florida phosphate rock was equilibated a second time with dilute HCl solutions. Table 16 shows the calculated pI_{FA} values. The average pI_{FA} values in the pH range in which the average pI_{CA} values were calculated are shown in Table 17. The solutions equilibrated with the unextracted Florida phosphate rock were supersaturated with respect to fluorapatite regardless the ratio of solid to solution. The over-all average of pI_{FA} values which were in the content range in Table 16 for acid-extracted phosphate rock was 119.2, which is the same as the value reported by McCann (1968) for the negative logarithm of the solubility-product constant for fluorapatite and is comparable with the value of 119.7 obtained in experiment 7.

From the results in Table 17, it appears that the solutions were at equilibrium with both carbonate apatite and fluorapatite. The following theoretical considerations, however, point out a new complexity that reduces the certainty of the inferences.

Carbonate apatite may be represented conceptually as a solid solution of fluorapatite with ionic substitutions (i.e., $CO_3^{--} + F^-$ substituting for PO_4^{---}, and $Na^+ + Mg^{++}$ substituting for Ca^{++}), in which the mole fraction of fluorapatite, N_{FA}, is always <1. When there is no isomorphous substitution, N_{FA} is equal to 1, and the mineral is fluorapatite. When isomorphous substitution takes place. N_{FA} is less than 1, and the mineral is a carbonate apatite.

The solubility-product constant is meaningful only when it is expressed by the chemical formula of the solid with which the solution is equilibrated. Consequently the solubility-product constant for carbonate apatite is best expressed by the chemical formula of carbonate apatite itself. However, if carbonate apatite is a solid solution of fluorapatite with ionic isomorphous substitutions, the solution theoretically should also be at equilibrium with the molar fraction of fluorapatite. In other words, the solubility-product constant can also be expressed by the chemical formula of fluorapatite provided the solid solution behaves ideally. Thus,

$$K^1_{FA} = K_{FA} \cdot N_{FA} \tag{38}$$

where K^1_{FA} is the solubility-product constant for the fluorapatite part of the solid solution that constitutes carbonate apatite, K_{FA} is the true solubility-product constant for fluorapatite, and N_{FA} is the molar fraction of fluorapatite in the solid solution.

Taking the negative logarithm of both sides of equation 38,

$$pK^1_{FA} = pK_{FA} + pN_{FA} \tag{39}$$

In the case of pure fluorapatite,

$$N_{FA} = 1$$

and

$$pK_{FA} = 119.16 \text{ (McCann, 1968).}$$

Therefore,

$$pK^{1}_{FA} = 119.16.$$

In the case of Florida phosphate rock,

$$N_{FA} = 5.19/6.00 = 0.87$$

$$\therefore pK^{1}_{FA} = 119.26$$

In the case of phosphate rock, the maximum replacement of PO_4^{---} by CO_3^{--} is approximately 24%, which corresponds to the limiting substitution prediced by Pauling's critical ratio rule (McClellan and Lehr, 1969). Thus, the minimum molar fraction of fluorapatite is

$$N_{FA} = 0.76.$$

Therefore,

$$pK^{1}_{FA} = 119.32$$

It can be seen now that the $p^{1}K_{FA}$ value ranges from 119.16 (pure fluorapatite) to 119.32 (carbonate apatite with maximum ionic substitution). The range is too small to permit experimental study.

The practical consequence of these theoretical considerations is that, if carbonate apatite do behave as ideal solid solutions of carbonate apatite and fluroapatite, the apatite in all phosphate rocks would be expected to show, within experimental error, the solubility-product constant for fluorapatite. Empirical evidence to be shown in connection with experiment 10 indicates that the apatites in phosphate rocks are not to be regarded as a solid solution of fluorapatite and carbonate apatite, as supposed here, but rather as carbonate apatites.

Experiment 9. Solubility of Apatites in Unextracted and Citrate-extracted Phosphate Rocks

Introduction

Previous experiments indicated that a particular sample of Florida phosphate rock exhibits a constant ion-activity product or solubility-product constant within a certain range of pH. The objectives of this experiment were to determine other phosphate rocks would show a solubility behavior similar to that exhibited by the Florida phosphate rock studied in previous experiments and to determine whether the solubility is related to the degree of substitution of the apatite component.

Procedures

Five different phosphate rocks (MR-465, MR-467, MR-468, MR-469, and MR-505) were used. These samples were obtained through the courtesy of Dr. D. L. McCune, Tennessee Valley Authority, Muscle Shoals, Alabama.

The solubility measurements were made on the unextracted phosphate rocks and on samples that had been extracted with alkaline ammonium citrate solution. The citrate-extracted phosphate rocks were free from alkaline-earth carbonates, as indicated by methods of X-ray diffraction, infrared absorption, and optical mineralogy. The ratio of solid to solution in the equilibrations of the phosphate rocks with dilute HCl solutions was 1 g per 100 ml of solution. The equilibration temperature was maintained at 25° C for 30 days.

Results and discussion

MR-465 phosphate rock The results are given in Table 18 and Figure 23. In the case of the citrate-extracted phosphate rock, the values of pI_{CA} ranged from 118.4 to 118.9 at pH values $\geqslant 3.69$. The average was 118.7. For the unextracted phosphate rock, the pI_{CA} value steadily decreased as the pH increased.

The failure of the unextracted phosphate rock to show a pH range in which pI_{CA} was relatively constant appears to be a consequence of the alkaline-earth carbonate content of this particular phosphate rock. Alkaline-earth carbonates raise the pH of the solution after the dilute HCl has dissolved some of the apatite, and the solutions then tend to remain supersaturated with respect to the apatite. Further information on the alkaline-earth carbonate effect may be found in Appendix C. An accessory contributing factor that may aid in explaining the lowest pI_{CA} values at the highest pH values is increasing substitution of OH^- for F^- in the apatite with an increase in pH. McCann (1968) suggested this mechanism as a possible explanation for a decrease in the value of the negative logarithm of the ion-activity product of fluorapatite at pH values above 6.4 in studies with pure fluorapatite. The effect he observed, however, was far smaller than that shown in Figure 23.

Figure 24 shows a plot of $p[P]_T$ versus p[Ca] from Table 18. The theoretical line was based on the assumption that the dissolution of carbonate apatite in phosphate rock was stoichiometric, i.e., the ratio of $[P]_T/[Ca]$ in the equilibrated solution was the same as that in the carbonate apatite. In the case of MR-465, the mole ratio of $[P]_T/[Ca]$ in the carbonate apatite with the formula of $Ca_{9.83}Na_{0.12}Mg_{0.05}(PO_4)_{0.50}F_{2.20}$

Table 18. Negative logarithm of ionic concentrations, ionic activities, and ion-activity products for carbonate apatite when MR-465 phosphate rock was equilibrated with dilute HCl solutions at 25° C for 30 days

Sample no.	pH	p[Ca]	$p[P]_T$	p[Na]	p[Mg]	pF	pI_{CA} [a]
			Unextracted phosphate rock				
1	3.29	1.734	2.135	3.18	3.28	3.52	120.2
2	4.12	2.060	2.495	3.46	3.36	3.52	114.4
3	4.12	2.058	2.474	3.50	3.32	3.70	114.7
4	5.30	2.465	2.950	3.74	3.48	3.55	106.0
5	6.70	2.986	3.911	4.00	3.58	3.98	100.9
6	6.97	3.110	4.370	3.99	3.59	4.05	102.0
			Citrate-extracted phosphate rock				
1	3.30	1.731	2.053	3.14	4.03	3.56	119.8
2	3.69	2.049	2.371	3.42	4.31	3.45	118.7
3	3.98	2.320	2.679	3.73	4.49	3.35	118.8
4	4.87	2.980	3.332	4.56	4.97	3.82	118.4
5	5.19	3.243	3.609	4.79	4.97	4.00	118.9
6	5.20	3.220	3.578	4.79	4.88	4.02	118.4
7	5.59	3.558	3.850	4.99	5.00	4.05	118.9

[a] $pI_{CA} = 9.83\ pCa + 0.12\ pNa + 0.05\ pMg + 5.54\ pPO_4 + 0.50\ pCO_3 + 2.20\ pF.$

was 5.54/9.83. Therefore, the following equation was used to construct the theoretical line in Figure 24:

$$p[P]_T = 0.25 + p[Ca] \qquad (40)$$

As compared with the unextracted MR-465 phosphate rock, the points of the citrate-extracted MR-465 phosphate rock were close to the theoretical line. Failure to follow the theoretical pattern of stoichiometric dissolution when only a small proportion of the solid has dissolved seems to be a characteristic of finely divided apatites (Wier, 1968; McCann,

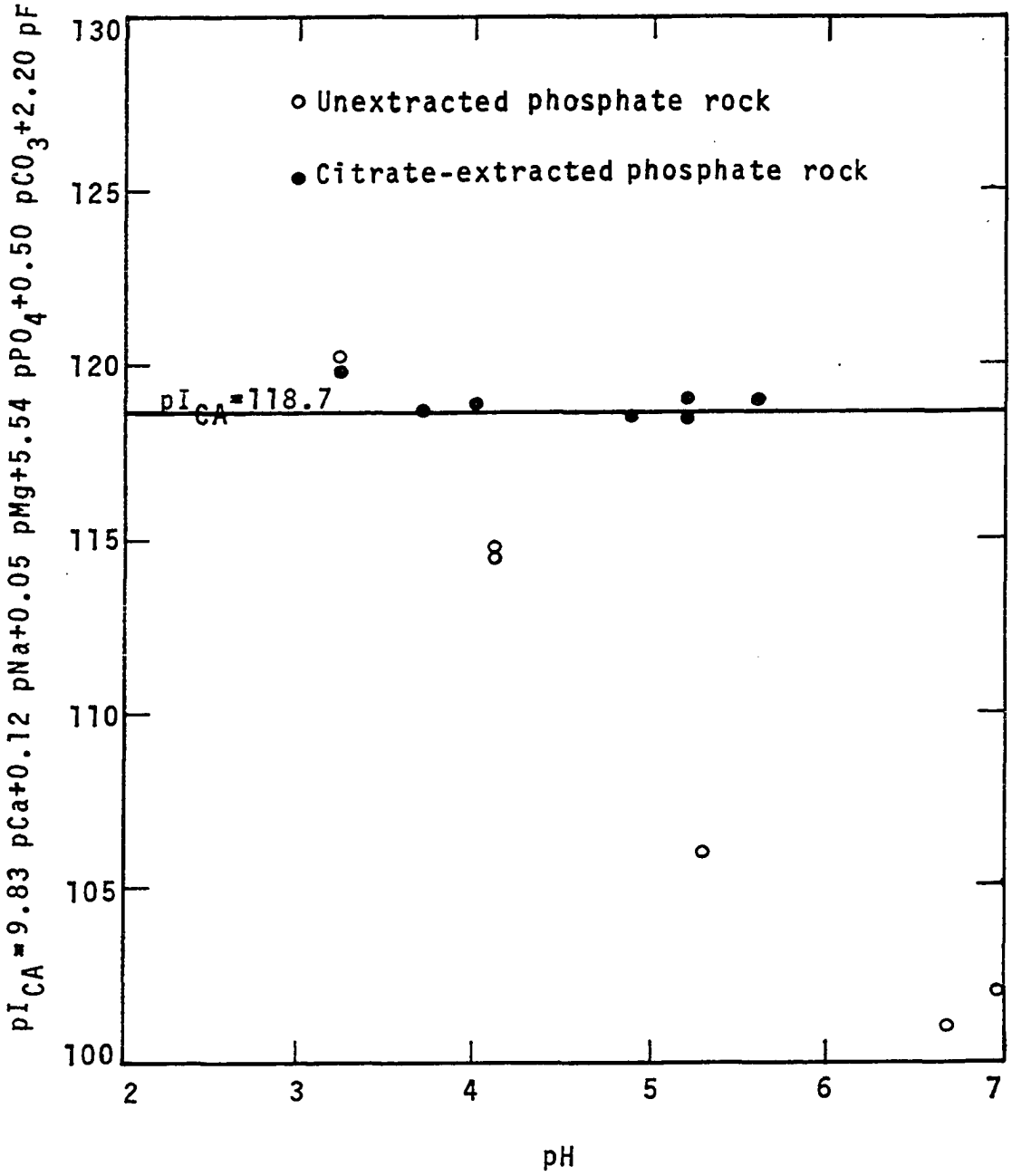

Figure 23. Negative logarithm of ion-activity product of carbonate apatite versus pH in solutions obtained in equilibrations of unextracted and citrate-extracted MR-465 phosphate rock with dilute solutions of hydrochloric acid for 30 days at 25° C

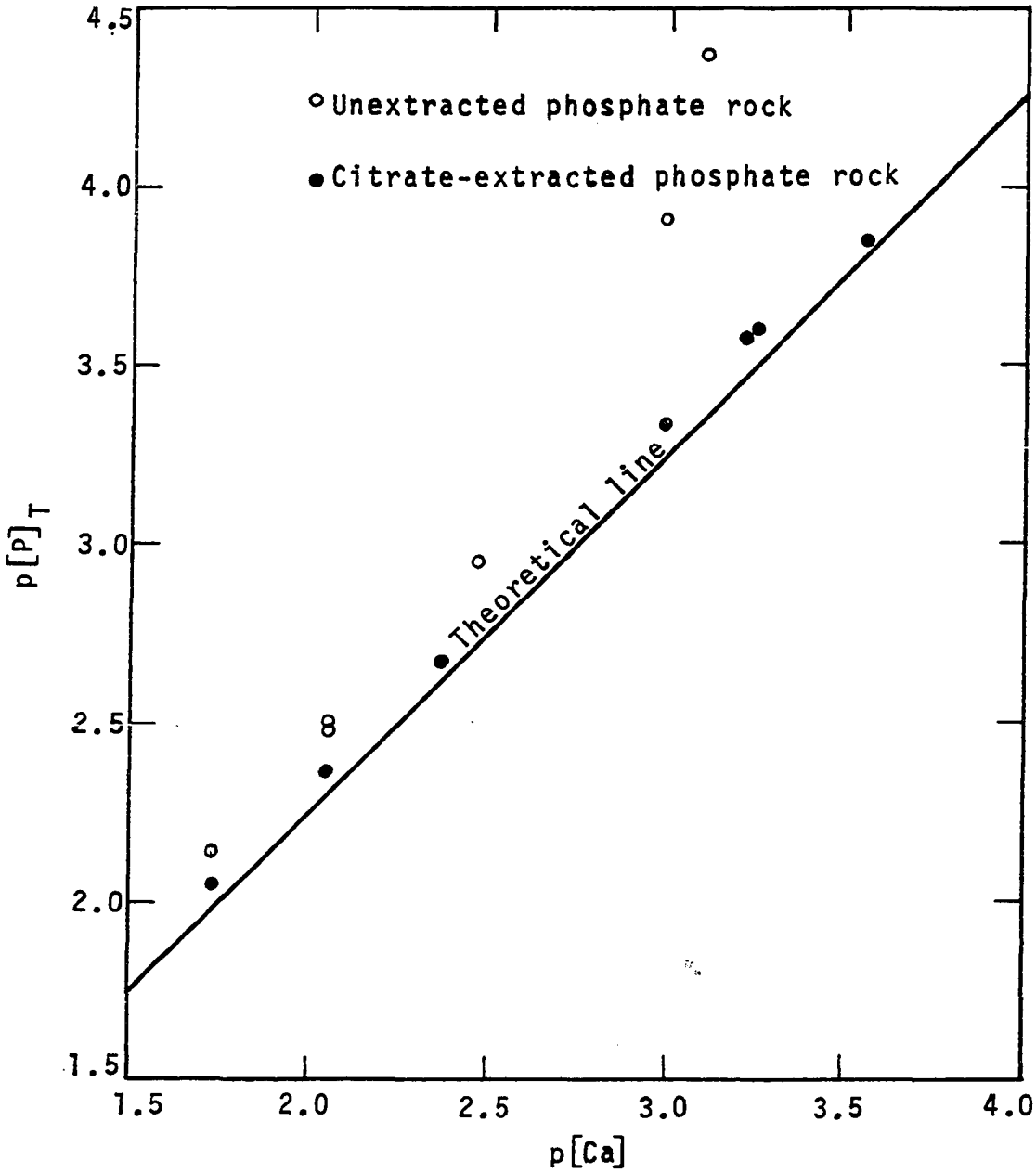

Figure 24. Plot of $p[P]_T$ versus p[Ca] of solutions after equilibration of unextracted and citrate-extracted MR-465 phosphate rock with different concentrations of dilute hydrochloric acid for 30 days at 25° C

1968; Avnimelech et al., 1970). This behavior has been attributed to the tendency of the solid to adsorb certain ions preferentially from the solution.

MR-467 phosphate rock The results are given in Table 19 and Figure 25. In Figure 25, an average pI_{CA} value of 114.4 was obtained within the pH range from 4.6 to 5.7 for the citrate-extracted MR-467 phosphate rock. Within this pH interval, the pI_{CA} values were relatively constant, ranging from 114.1 to 114.9.

The solubility value obtained with unextracted MR-467 phosphate rock at pH 5.34 (pI_{CA} = 114.0) was very close to the horizontal line of pI_{CA} = 114.4, as shown in Figure 25, but this was the only point in the pH range in which a constant ion-activity product usually occurred, and consequently no conclusions may be drawn. At low pH values, the unextracted phosphate rock exhibited the same trend of solubility as did the citrate-extracted phosphate rock. The results show that the presence of 0.4% CO_2 as alkaline-earth carbonate in this sample had no effect on the ion-activity product of the carbonate apatite at the low pH values.

MR-468 phosphate rock The results are given in Table 20 and Figure 26. This phosphate rock did not contain detectable quantities of alkaline-earth carbonates. It was expected, therefore, that the unextracted phosphate rock might exhibit a constant ion-activity product within a limited pH range. Figure 26 shows that the pI_{CA} values ranged from 118.3 to 119.5 with an average value of 118.7 at pH $\geqslant$ 4.24 for the unextracted and citrate-extracted phosphate rocks. It is not certain why the solubility of the citrate-extracted phosphate rock was slightly higher (lower pI_{CA} values) than that of the unextracted phosphate rock at the low pH

Table 19. Negative logarithm of ionic concentrations, ionic activities, and ion-activity products for carbonate apatite when MR-467 phosphate rock was equilibrated with dilute HCl solutions at 25° C for 30 days

Sample no.	pH	p[Ca]	$p[P]_T$	p[Na]	p[Mg]	pF	pI_{CA}[a]
			Unextracted phosphate rock				
1	3.47	1.474	1.938	2.93	3.14	3.78	117.8
2	3.91	1.775	2.334	3.18	3.30	3.85	116.5
3	4.42	2.109	2.950	3.37	3.47	3.85	115.6
4	4.44	2.113	2.966	3.37	3.47	3.85	115.5
5	5.34	2.465	4.145	3.67	3.66	4.22	114.0
6	7.20	2.804	5.651	3.98	3.85	4.05	104.6
7	7.32	2.804	6.143	3.98	3.85	4.14	103.5
			Citrate-extracted phosphate rock				
1	3.41	1.469	1.837	2.90	3.31	3.70	117.9
2	3.76	1.782	2.192	3.14	3.57	3.62	117.1
3	4.11	2.081	2.521	3.43	3.77	3.50	116.3
4	4.66	2.436	2.928	3.74	4.06	3.50	114.4
5	5.28	2.887	3.533	3.96	4.35	4.00	114.9
6	5.53	2.989	3.752	4.06	4.42	4.15	114.3
7	5.59	3.021	3.803	4.11	4.45	4.15	114.1
8	5.71	3.107	4.096	4.15	4.48	4.00	114.5

[a] $pI_{CA} = 9.54\ pCa + 0.33\ pNa + 0.13\ pMg + 4.80\ pPO_4 + 1.20\ pCO_3 + 2.48\ pF$.

values (pH < 4.24).

It is of interest to note that the solubility of MR-468 phosphate rock is the same as that of MR-465 phosphate rock. The average pI_{CA} value is 118.7 in both instances. These two phosphate rocks are known to be similar as regards the chemical compositions of their carbonate apatites.

MR-469 phosphate rock The results are given in Table 21 and Figure 27. This phosphate rock was metamorphic rather than sedimentary. It contained no detectable amount of alkaline-earth carbonate. Figure 27 shows the similarity of the solubility of the unextracted and citrate-

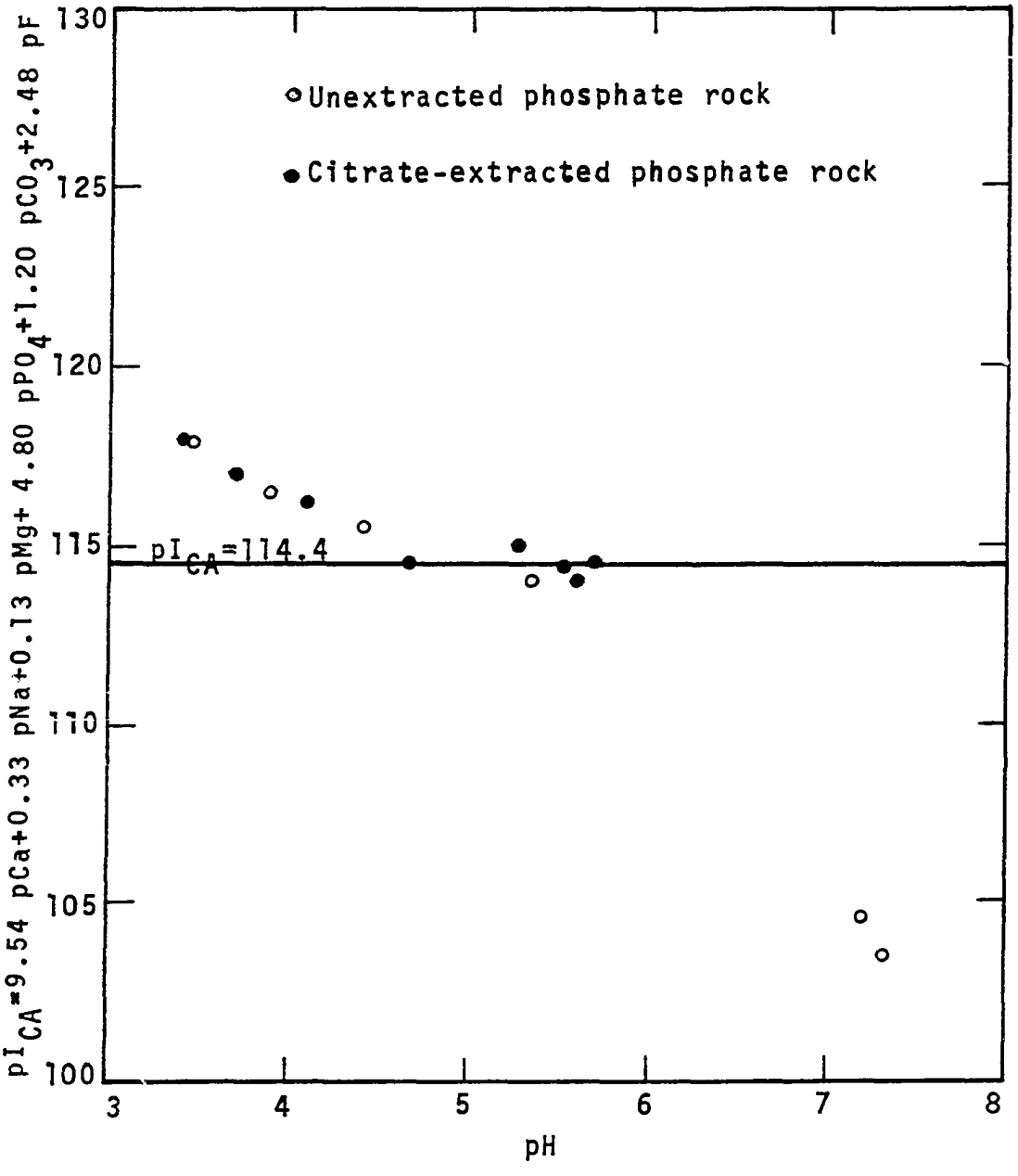

Figure 25. Plot of negative logarithm of ion-activity product for carbonate apatite versus pH of solutions after equilibration of unextracted and citrate-extracted MR-467 phosphate rock with different concentrations of dilute hydrochloric acid at 25° C for 30 days

Table 20. Negative logarithm of ionic concentrations, ionic activities, and ion-activity products for carbonate apatite when MR-468 phosphate rock was equilibrated with dilute HCl solutions at 25° C for 30 days

Sample no.	pH	p[Ca]	$p[P]_T$	p[Na]	p[Mg]	pF	pI_{CA} [a]
			Unextracted phosphate rock				
1	2.52	1.530	1.906	3.39	3.77	4.00	128.4
2	3.02	1.789	2.180	3.59	3.98	4.18	125.6
3	3.62	2.114	2.518	4.16	4.23	4.30	122.7
4	3.62	2.109	2.529	4.19	4.25	4.30	122.8
5	4.38	2.506	2.930	4.46	4.44	4.18	118.7
6	5.30	3.124	3.693	4.70	4.68	4.34	118.3
7	5.62	3.323	4.159	4.75	4.75	4.34	117.7
8	5.84	3.466	4.619	4.79	4.80	4.30	119.5
			Citrate-extracted phosphate rock				
1	2.47	1.514	1.866	3.36	3.84	3.65	128.0
2	2.96	1.785	2.150	3.67	4.08	3.62	125.0
3	3.52	2.082	2.432	4.07	4.38	3.70	121.9
4	4.24	2.431	2.812	4.47	4.84	3.80	118.3
5	5.01	3.056	3.426	5.06	5.39	4.10	118.6
6	5.33	3.306	3.743	5.02	5.47	4.28	119.2
7	5.34	3.343	3.752	4.87	5.50	4.28	119.5
8	5.69	3.546	4.005	5.29	5.61	4.18	118.5

[a] $pI_{CA} = 9.85\ pCa + 0.11\ pNa + 0.04\ pMg + 5.56\ pPO_4 + 0.44\ pCO_3 + 2.18\ pF.$

extracted samples at pH $\leqslant$ 5.08. An average pI_{CA} value of 121.2 was obtained within the range of pH 4.01-5.08. Only one of the ion-activity products for the unextracted phosphate rock fell within the critical pH range, however, and so it is not clear whether the unextracted phosphate rock did or did not have a constant ion-activity product.

MR-505 phosphate rock The results are given in Table 22 and Figure 28. This phosphate rock was of igneous origin, and the apatite component was in the form of fluorapatite with the formula of

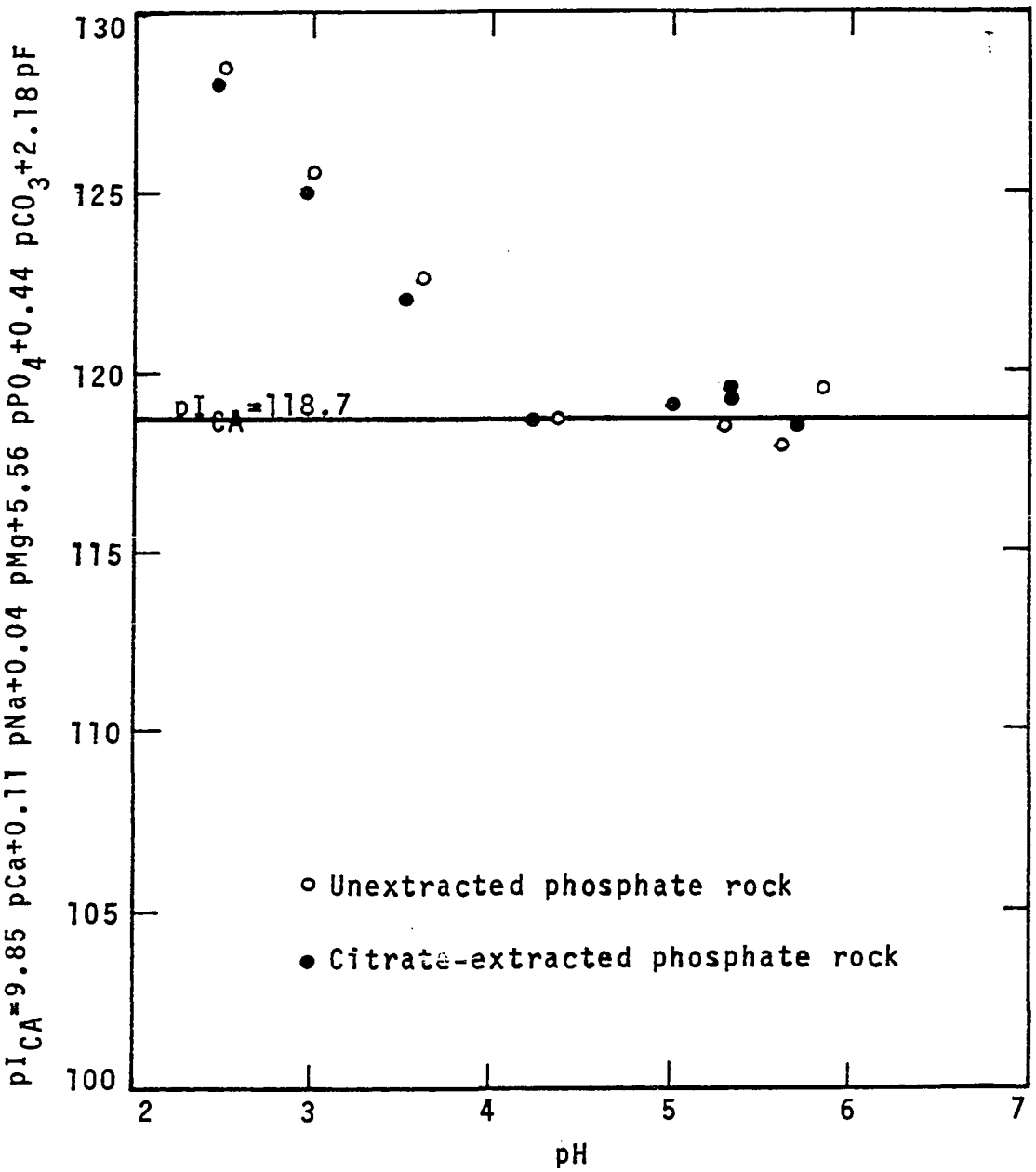

Figure 26. Plot of negative logarithm of ion-activity product of carbonate apatite versus pH of solutions after equilibration of unextracted and citrate-extracted MR-468 phosphate rock with different concentrations of dilute hydrochloric acid at 25° C for 30 days

Table 21. Negative logarithm of ionic concentrations, ionic activities, and ion activity products for carbonate apatite when MR-469 phosphate rock was equilibrated with dilute HCl solutions at 25°C for 30 days

Sample no.	pH	p[Ca]	$p[P]_T$	p[Na]	p[Mg]	pF	pI_{CA} [a]
			Unextracted phosphate rock				
1	2.18	1.612	1.962	3.49	3.15	3.90	132.9
2	2.47	1.877	2.242	3.54	3.34	3.95	132.4
3	2.97	2.168	2.529	3.52	3.58	3.90	129.7
4	2.97	2.168	2.530	3.56	3.61	4.05	130.0
5	4.01	2.513	2.837	3.65	3.85	3.82	121.3
6	5.85	3.109	3.694	3.75	4.03	4.28	110.5
7	5.99	3.225	3.680	3.76	4.09	4.40	110.2
			Citrate-extracted phosphate rock				
1	2.22	1.588	1.919	4.65	3.21	3.79	131.8
2	2.50	1.880	2.222	4.81	3.41	3.75	131.6
3	3.22	2.298	2.609	5.09	3.91	3.65	127.6
4	3.64	2.433	2.726	4.94	4.12	3.62	124.1
5	4.64	2.988	3.294	5.20	4.20	3.79	120.5
6	5.01	3.281	3.604	5.30	4.95	3.98	121.0
7	5.04	3.348	3.669	5.50	4.98	4.00	121.7
8	5.08	3.658	3.990	5.62	5.11	4.05	121.4

[a] $pI_{CA} = 9.93\ pCa + 0.05\ pNa + 0.02\ pMg + 5.77\ pPO_4 + 0.23\ pCO_3 + 2.09\ pF.$

$Ca_{10}(PO_4)_6F_2$ (McClellan and Lehr, 1969). For the citrate-extracted phosphate rock, an average pI_{FA} value of 133.3 was obtained within the pH interval of 4.01 to 5.04. The pI_{FA} values ranged from 129.6 to 135.8 within this pH interval, which is a greater variation than was obtained with any other phosphate rock.

With the unextracted MR-505 phosphate rock, the ion-activity product of fluorapatite was a function of pH, and no constant ion-activity product

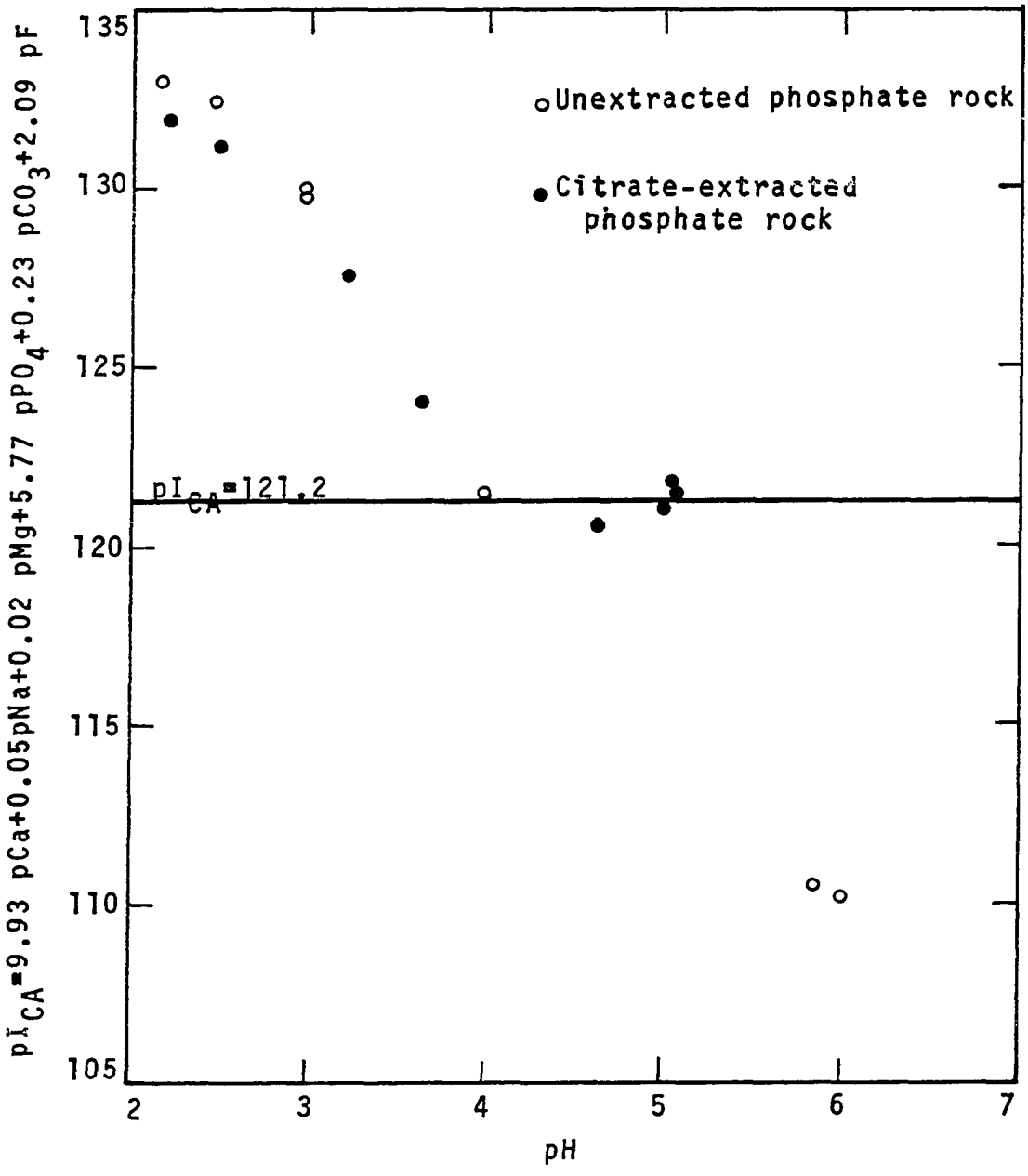

Figure 27. Plot of negative logarithm of ion-activity product of carbonate apatite versus pH of solutions after equilibration of unextracted and citrate-extracted MR-469 phosphate rock with different concentrations of dilute hydrochloric acid at 25° C for 30 days

Table 22. Negative logarithm of ionic concentrations, ionic activities, and ion-activity products for fluorapatite when MR-505 phosphate rock was equilibrated with dilute HCl solutions at 25° C for 30 days

Sample no.	pH	p[Ca]	$p[P]_T$	p[Na]	p[Mg]	pF	pI_{FA} [a]
			Unextracted phosphate rock				
1	1.92	1.761	1.789	3.12	3.09	4.48	137.6
2	2.43	1.971	2.565	3.85	3.24	4.67	136.7
3	4.95	2.191	3.282	3.97	3.77	4.23	110.7
4	5.24	2.315	3.296	3.89	3.98	4.18	108.2
5	5.98	2.539	3.721	4.34	4.32	4.05	103.7
6	7.12	2.892	4.516	4.48	5.11	4.28	100.3
7	7.36	2.913	4.875	4.51	5.15	4.28	100.6
8	7.57	2.913	5.271	4.56	5.19	4.05	101.0
			Citrate-extracted phosphate rock				
1	2.11	2.172	2.504	4.29	3.31	4.50	142.1
2	2.39	2.480	2.837	4.44	3.43	4.84	143.2
3	2.94	2.760	3.126	4.70	3.60	4.80	140.0
4	4.01	3.191	3.545	4.95	4.51	4.73	133.2
5	4.39	3.513	3.907	4.99	4.59	4.73	133.8
6	4.47	3.460	3.850	5.15	4.57	4.66	131.9
7	4.62	3.503	3.738	4.76	4.55	4.65	129.6
8	4.93	4.093	4.347	4.98	4.97	4.65	135.7
9	5.04	4.225	4.510	4.91	5.09	4.40	135.8

[a] $pI_{FA} = 10pCa + 6pPO_4 + 2pF$.

was obtained in any pH range; the distribution of points, however, was not such as to provide assurance that no constant value existed. At higher pH values ($\geq$4.95), the solutions were supersaturated with respect to pure synthetic fluorapatite prepared by McCann (1968). This behavior might be expected on the basis that MR-505 phosphate rock contained 2.6% CO_2 as alkaline-earth carbonates. The presence of alkaline-earth

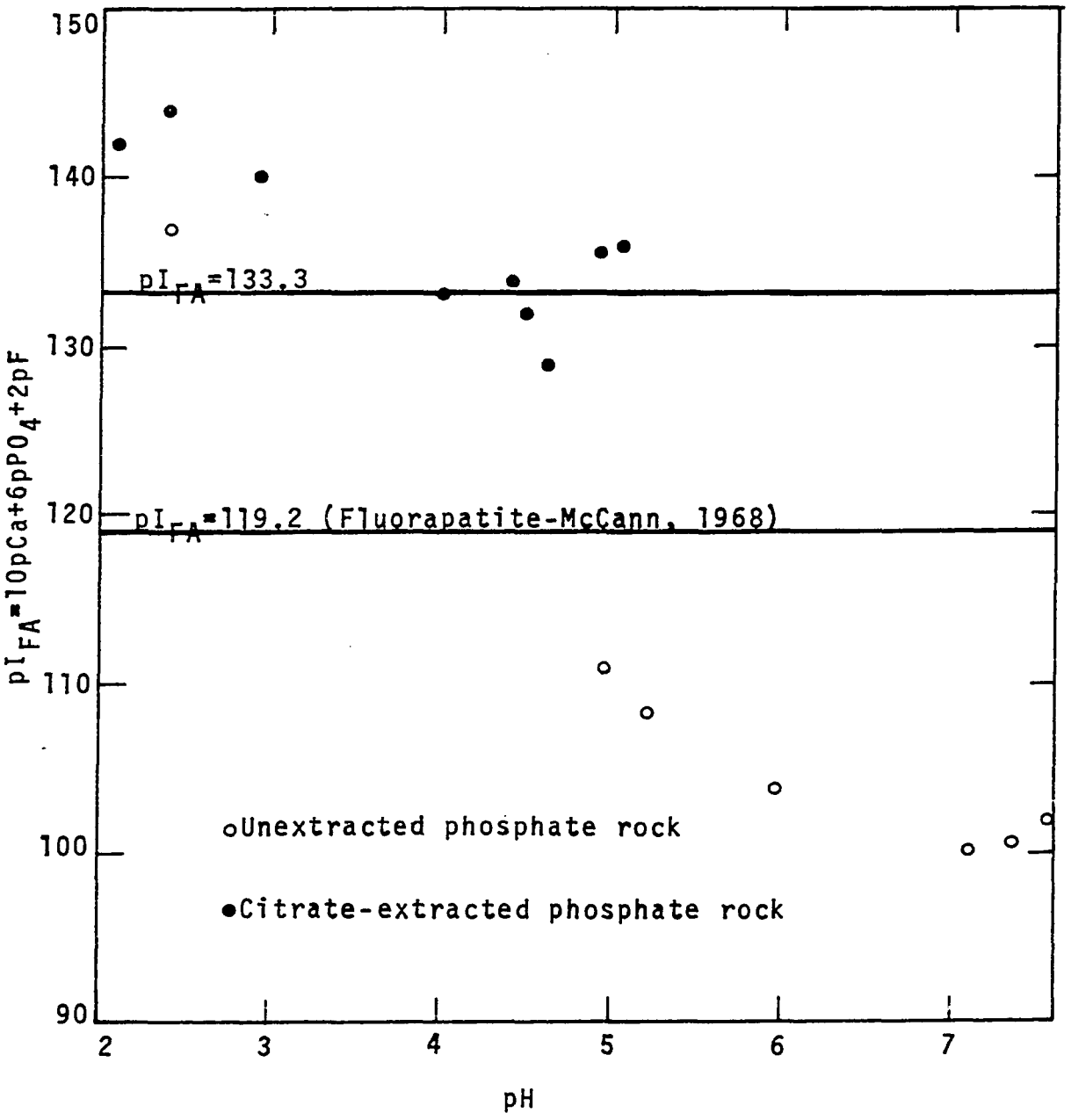

Figure 28. Plot of negative logarithm of ion-activity product of fluorapatite versus pH of solutions after equilibration of unextracted and citrate-extracted MR-505 phosphate rock with different concentrations of dilute hydrochloric acid at 25° C for 30 days

carbonates was easily detected by methods of X-ray diffraction, infrared absorption, and optical mineralogy.

The average value of 133.3 calculated for the negative logarithm of the ion-activity product of fluorapatite for sample MR-505 is much higher than that of 119.2 reported by McCann (1968) for the synthetic fluorapatite. Working on another igneous fluorapatite from Quebec, Wier (1968) observed an average pI_{FA} value of 124.0 within the range of pH 3.74 to 4.90. Thus, like the solutions equilibrated with the fluorapatite in phosphate rock sample MR-505, the solutions equilibrated with the Quebec fluorapatite exhibited unsaturation with respect to the synthetic fluorapatite.

One possible explanation of the results is that the solutions equilibrated with igneous fluorapatites did not reach equilibrium in the 30-day period of equilibration used with phosphate rock MR-505 or in the 71-day period of equilibration used by Wier (1968) with the Quebec fluorapatite. Another possible explanation is that the various fluorapatites had different activities. Naturally occurring igneous fluorapatite would be expected to have lower activity than that of synthetic fluorapatite because of better crystallinity.

General discussion

To compare the solubility of various phosphate rocks was the second objective in this experiment. There are many ways to compare the solubility of phosphate rocks. Lehr et al. (1967) measured the time required to dissolve a certain amount of phosphate rock in a strong acid as an index of chemical reactivity. In a recent paper, Lehr and McClellan (1972) proposed the concept of ACS (absolute citrate solubility percen-

tage) as an index to compare the solubility of various phosphate rocks.

A disadvantage of the first method is that it is a kinetic measurement rather than an equilibrium measurement. Moreover, although dissolution of phosphate rocks by a relatively concentrated solution of a strong acid may provide a valuable characterization of the reactivity of these rocks in the manufacture of fertilizers by a similar process, the dissolution process in the soil involves different circumstances and may be controlled by different factors. Characterizations obtained by the second method (ACS index) have been found to have a high correlation with the responses of crops to additions of phosphate rocks to soils in the greenhouse (Lehr and McClellan, 1972). Nevertheless, the chemistry of dissolution of phosphate rock by a citrate solution is not similar to the natural processes of dissolution of phosphate rock in soils.

When phosphate rocks are equilibrated with dilute HCl solution, a variety of methods may be used to provide an index of the solubility. Three methods that may have some relevance to the matter of the comparative value of various phosphate rocks for application to soils as a source of phosphorus for plants are described in following paragraphs.

One method is to plot the concentration of phosphorus in the equilibrated solutions against pH for various phosphate rocks. Figure 29 shows such a plot of data obtained in solubility studies with five different phosphate rocks which have been extracted by alkaline ammonium citrate solution to remove alkaline-earth carbonates. Below pH 4.3, the total phosphorus concentrations yielded by the various phosphate rocks are in the order, MR-467 > MR-465 > MR-468 > MR-469 > MR-505. Above pH 4.3, the order is MR-467 > MR-465, MR-468 > MR-469 > MR-505. The order is the

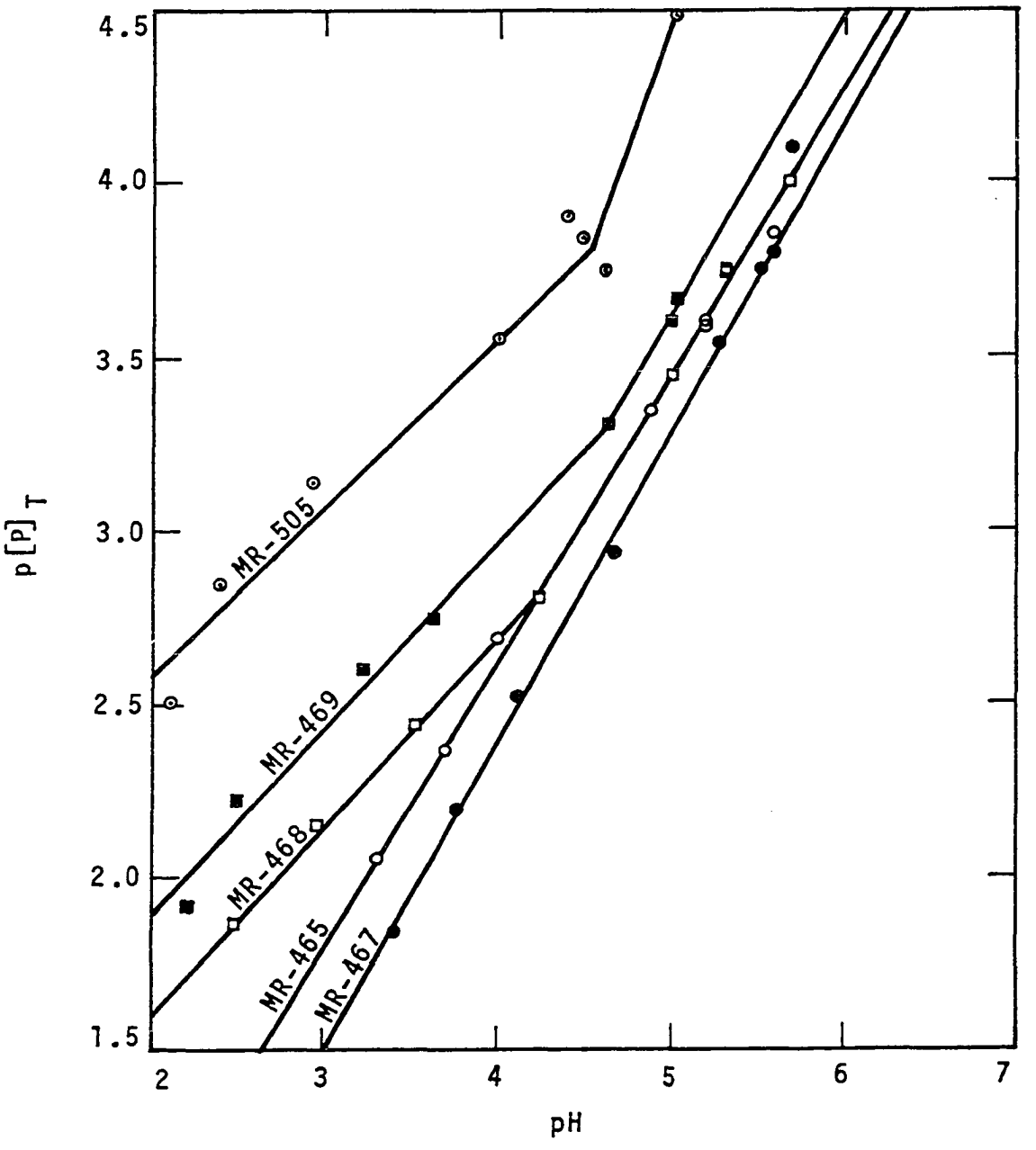

Figure 29. Plot of negative logarithm of phosphorus concentration versus pH of solutions obtained in equilibrations of citrate-extracted phosphate rocks with dilute solutions of hydrochloric acid for 30 days at 25° C

same as that of the degree of substitution of carbonate for phosphate in the apatite structure. The number of moles of carbonate per mole of apatite in the various phosphate rocks are 1.20, 0.50, 0.44, 0.23, and 0 for MR-467, MR-465, MR-468, MR-469, and MR-505, respectively. This trend indicates that the substitution of carbonate for phosphate affects the solubility of phosphate rocks. Lehr and McClellan (1972) made similar findings on the basis of measurements of citrate-soluble phosphorus.

A second method is to compare the ion-activity products of the carbonate apatites obtained in the pH range where the values were constant and hence may be called solubility-product constants. Figure 30 shows a plot of the negative logarithm of the solubility-product constants (pK) of the apatites in various phosphate rocks, together with that of synthetic fluorapatite (McCann, 1968), as a function of the number of moles of carbonate per mole of apatite. The trend of the points indicates that carbonate-substitution decreases the pK values, which means that the solubility-product constants and the solubility are increased. However, synthetic fluorapatite exhibited a lower pK value (pK_{FA} = 119.2) than did MR-469 phosphate rock (pK_{CA} = 121.2) even though the latter had 0.23 mole of carbonate per mole of apatite. Furthermore, MR-505 phosphate rock had a much higher pK value (pK_{FA} = 133.3) than did synthetic fluorapatite. The apatite in MR-505 phosphate rock was known to have the chemical composition of fluorapatite (McClellan and Lehr, 1969). A theoretical difficulty with this method of representing solubilities is that the numbers representing the solubility-product constants of differently substituted phosphate rocks are not directly comparable in terms of relative solubilities.

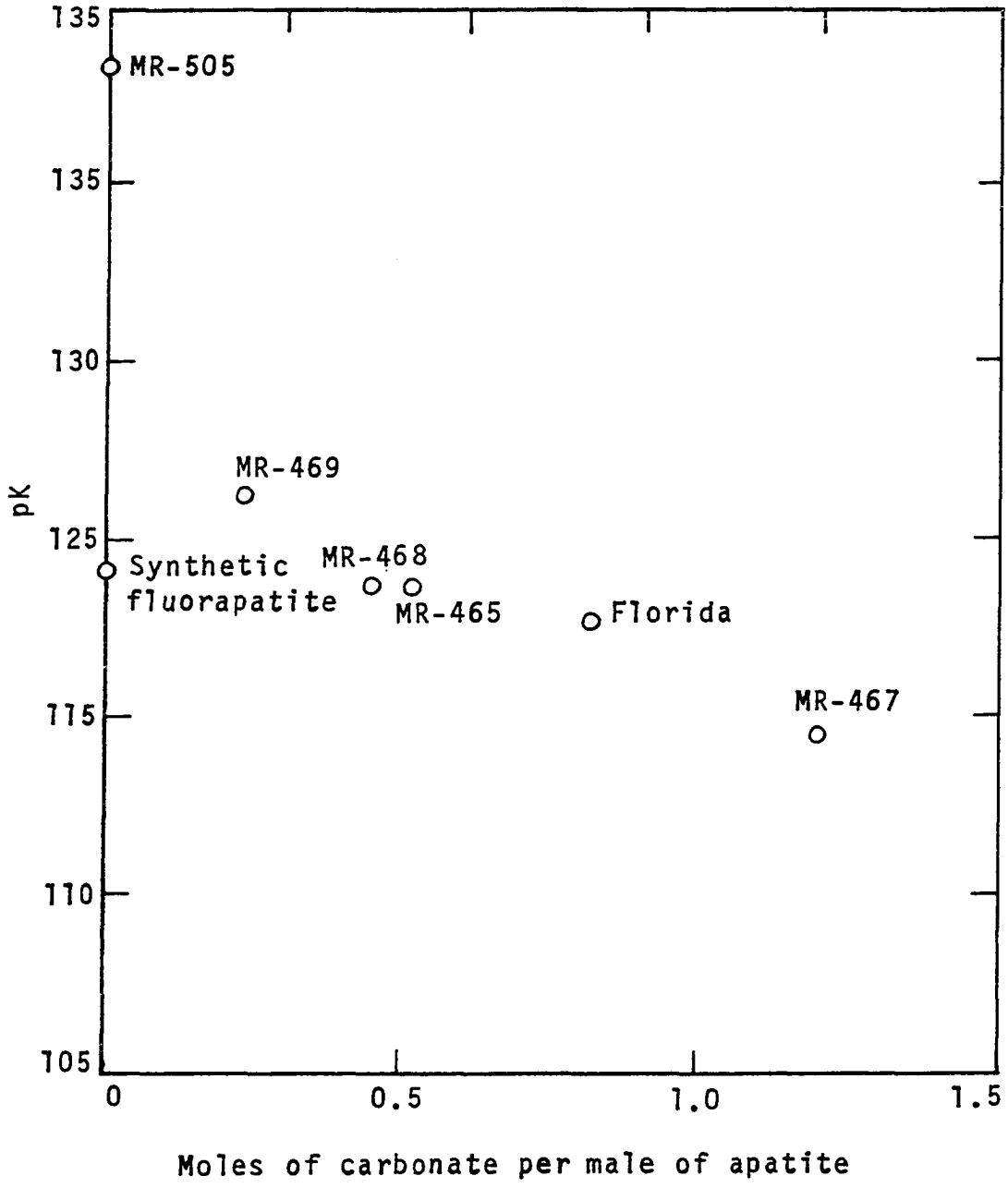

Figure 30. Plot of negative logarithm of solubility-product constant versus number of moles of carbonate per mole of apatite in various phosphate rocks and synthetic fluorapatite

To eliminate the problem in the second method, a third method may be used. In the section of Theoretical Background, a concept of free energy of formation was proposed to express the activity of a particular apatite. The general formula of a carbonate apatite may be expressed as

$$Ca_aNa_bMg_c(PO_4)_d(CO_3)_xF_y$$

In accordance with this formula, equation 21 (page 36) may be expressed more explicitly as equation 41:

$$\Delta G^o_{f,CA} = a\Delta G^o_{f,Ca^{++}} + b\Delta G^o_{f,Na^+} + c\Delta G^o_{f,Mg^{++}} + d\Delta G^o_{f,PO_4^{---}} + x\Delta G^o_{f,CO_3^{--}} + y\Delta G^o_{f,F^-} + RT\ln K \qquad (41)$$

The free energy of formation of a particular carbonate apatite, $\Delta G^o_{f,CA}$, can be calculated provided that its solubility-product constant, K, is known. The required values of ΔG^o_f for the ions in equation 41 are given by Rossini et al. (1952), and they were shown on page 38. Table 23 records the calculated values of $\Delta G^o_{f,CA}$ for the apatites in the various phosphate rocks.

One may note from Table 23 that the free energy of formation becomes less negative as the number of moles of carbonate per mole of apatite increases except for MR-505 phosphate rock and synthetic fluorapatite. These two samples both had the chemical composition of fluorapatite, $CA_{10}(PO_4)_6F_2$, yet they exhibited different free energies of formation.

In the section on Theoretical Background, a theoretical equation was derived to show a linear relationship between the free energy of formation, $\Delta G^o_{f,CA}$, and the number of moles of carbonate per mole of apatite, X, as equation 29,

Table 23. Number of moles of carbonate per mole of apatite, negative logarithm of the solubility-product constant, and free energy of formation for various carbonate apatites in phosphate rocks and synthetic fluorapatite at 25° C

Sample	Number of moles of carbonate per mole of apatite	-log K	$\Delta G^{o}_{f,CA}$ (Kcal/mole)
MR-467	1.20	114.4	-2943.8
Florida	0.81	117.7	-2994.3
MR-465	0.50	118.7	-3035.6
MR-468	0.44	118.7	-3037.6
MR-469	0.23	121.2	-3064.6
Synthetic fluorapatite	0	119.2[a]	-3087.3
MR-505	0	133.3	-3107.2

[a]Data from McCann (1968).

$$\Delta G^{o}_{f,CA} = -3087.3 + (139.8 + 0.6k)X, \quad (29)$$

where k is a constant. A plot of $\Delta G^{o}_{f,CA}$ values from Table 23 against the number of moles of carbonate per mole of apatite for various phosphate rocks and synthetic fluorapatite is shown in Figure 31 (the values for synthetic fluorapatite and sample MR-505 were not used in computing the regression). A good linear regression line was obtained from the data of all the citrate-extracted phosphate rocks except MR-505. The linear regression was obtained as

$$\Delta G^{o}_{f,CA} = -3091.1 + 120.5X. \quad (42)$$

The observed value of the intercept in equation 42 is close to the theoretical value at X = 0 in equation 29, which was derived with use of the solubility-product constant for synthetic fluorapatite.

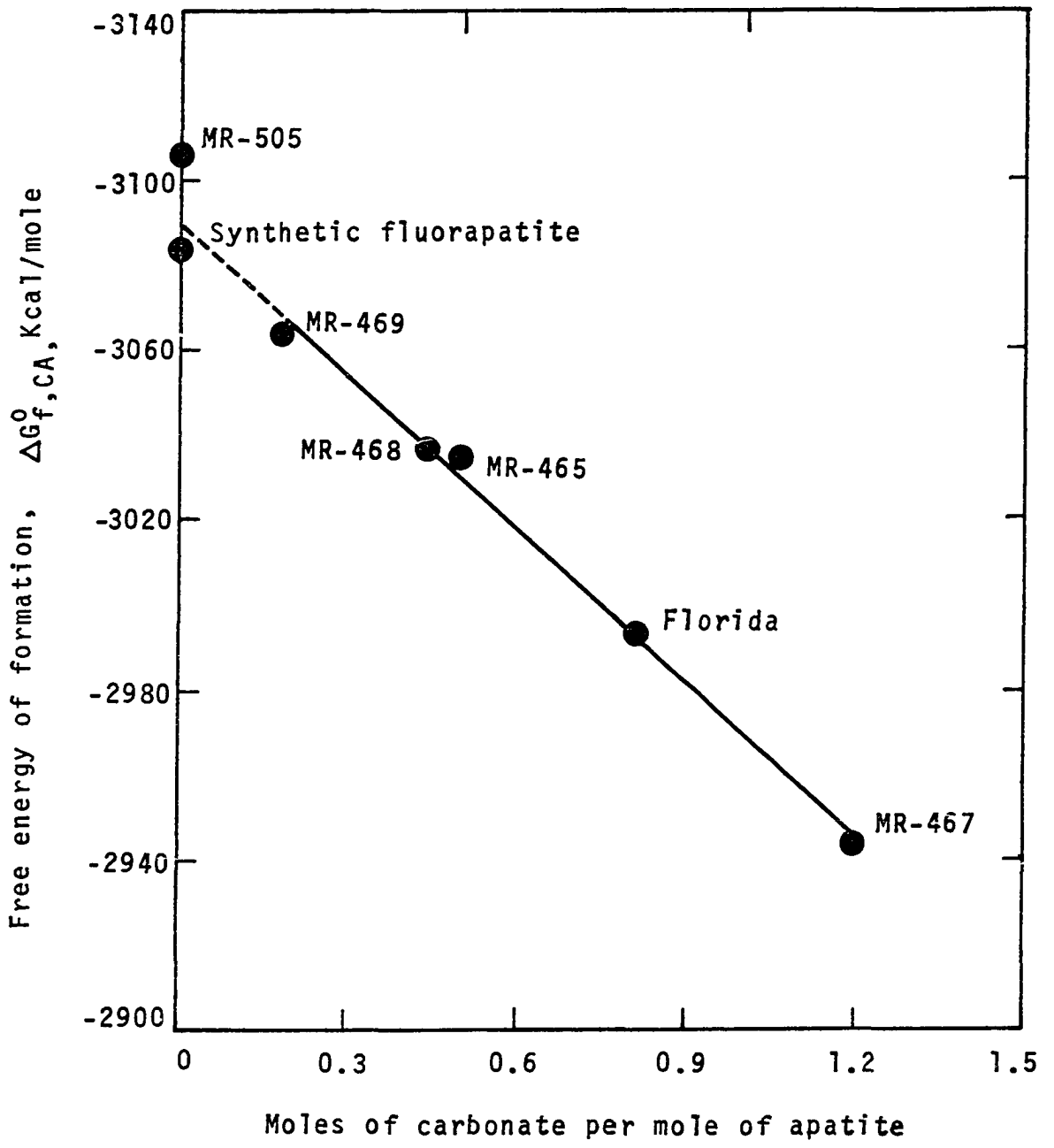

Figure 31. Plot of free energy of formation of apatites at 25° C versus number of moles of carbonate per mole of apatite in phosphate rocks and synthetic fluorapatite

Experiment 10. Solubility of Apatites in Acid-Extracted Phosphate Rocks

Introduction

In Experiment 8, it was found that the solubility of carbonate apatite in Florida phosphate rock decreased after acid treatment. In solubility studies on the acid-extracted material, the calculated values for the negative logarithm of the ion-activity products in the pH range in which constant values were obtained were 120.3 and 119.2 when expressed in terms of the formulas for carbonate apatite and fluorapatite, respectively. McCann (1968) reported the value for synthetic fluorapatite as 119.2. Therefore, it appears that the solutions were at equilibrium with both carbonate apatite and fluorapatite. There is also the possibility that the apatite is a solid solution of fluorapatite and carbonate apatite; and, if such is actually the case, the molar fraction of fluorapatite in the solid solution is near enough to unity that the ion-activity product for fluorapatite cannot be distinguished experimentally from the product of the molar fraction and the ion-activity product.

The first objective of this experiment was to investigate these problems with some other phosphate rocks. The second objective was to determine whether the solubilities exhibited by the citrate-extracted phosphate rocks used in experiment 9 would decrease when the phosphate rocks were extracted with dilute hydrochloric acid. If so, what would then be the relationship between the free energy of formation and carbonate substitution?

Procedure

Three different phosphate rocks, MR-467, MR-468, and MR-469, were used. The acid-extraction process was the same as described in experiment 8. Four periods of extraction were performed. The proportions of the various phosphate rocks extracted were estimated approximately as 26%, 20%, and 28% for MR-467, MR-468, and MR-469, respectively.

The solubility measurement was the same as in the previous experiments. The ratio of solid to solution was 1 g per 100 ml. The equilibration was at 25° C for 30 days.

Results and discussion

The results are given in Table 24. A plot of pI_{FA} versus pH of the equilibrated solutions is shown in Figure 32. None of the acid-extracted phosphate rocks exhibited the solubility-product constant of synthetic fluorapatite. The values for MR-467 corresponded to a condition of supersaturation, while those for MR-468 and MR-469 corresponded to unsaturation with respect to synthetic fluorapatite. These observations indicate that the solutions equilibrated with these phosphate rocks were not in equilibrium with newly formed fluorapatite or that, if they were, the newly formed fluorapatite exhibited a great range of activities or solubilities. The value of pK_{FA} = 119.2 obtained with the Florida phosphate rock in experiment 8 thus may have been a coincidence, with the solution actually in equilibrium with a carbonate apatite of low activity (pI_{CA} = 120.3).

The results obtained in this experiment also indicate that the apatite in phosphate rocks is not to be considered an ideal solid-solution of carbonate apatite and fluorapatite or, alternatively, that

Table 24. Negative logarithm of ionic concentrations, ionic activities, and ion-activity products for carbonate apatite and fluorapatite when three acid-extracted phosphate rocks were equilibrated with dilute HCl solutions at 25° C for 30 days

pH	p[Ca]	$p[P]_T$	p[Na]	p[Mg]	pF	pI_{CA} [a]	pI_{FA} [b]
			MR-467 phosphate rock				
3.80	2.078	2.347	3.55	3.98	3.38	119.0	116.4
4.02	2.292	2.580	3.75	4.16	3.38	119.0	116.5
4.47	2.751	2.959	4.17	4.48	3.36	118.8	117.2
4.56	2.833	3.036	4.16	4.54	3.34	118.5	116.7
			MR-468 phosphate rock				
3.30	2.142	2.421	3.96	4.39	3.76	125.0	125.0
3.57	2.383	2.653	4.26	4.70	3.72	124.8	123.9
4.30	3.092	3.254	4.62	5.05	3.88	125.7	125.1
4.47	3.297	3.426	4.76	5.12	3.86	126.4	125.4
			MR-469 phosphate rock				
2.83	2.210	2.491	3.72	3.79	3.72	131.1	130.8
3.20	2.428	2.703	3.61	4.06	3.74	129.4	129.1
5.02	3.896	3.942	5.09	5.20	4.00	128.2	128.1
5.07	4.021	4.003	5.14	5.19	4.00	128.9	128.9

[a] MR-467 phosphate rock, $pI_{CA} = 9.54pCa + 0.33pNa + 0.13pMg + 4.80pPO_4 + 1.20pCO_3 + 2.48pF$.
MR-468 phosphate rock, $pI_{CA} = 9.85pCa + 0.11pNa + 0.04pMg + 5.56pPO_4 + 0.44pCO_3 + 2.18pF$.
MR-469 phosphate rock, $pI_{CA} = 9.93pCa + 0.05pNa + 0.02pMg + 5.77pPO_4 + 0.23pCO_3 + 2.09pF$.

[b] $pI_{FA} = 10pCa + 6pPO_4 + 2pF$.

the ratio of the ion-activity product for fluorapatite to the mole fraction of fluorapatite in the solid solution is not equal to any constant value but varies among phosphate rocks. Thus, in Figure 32, the ion-activity products for fluorapatite for the three phosphate rocks cover a wide

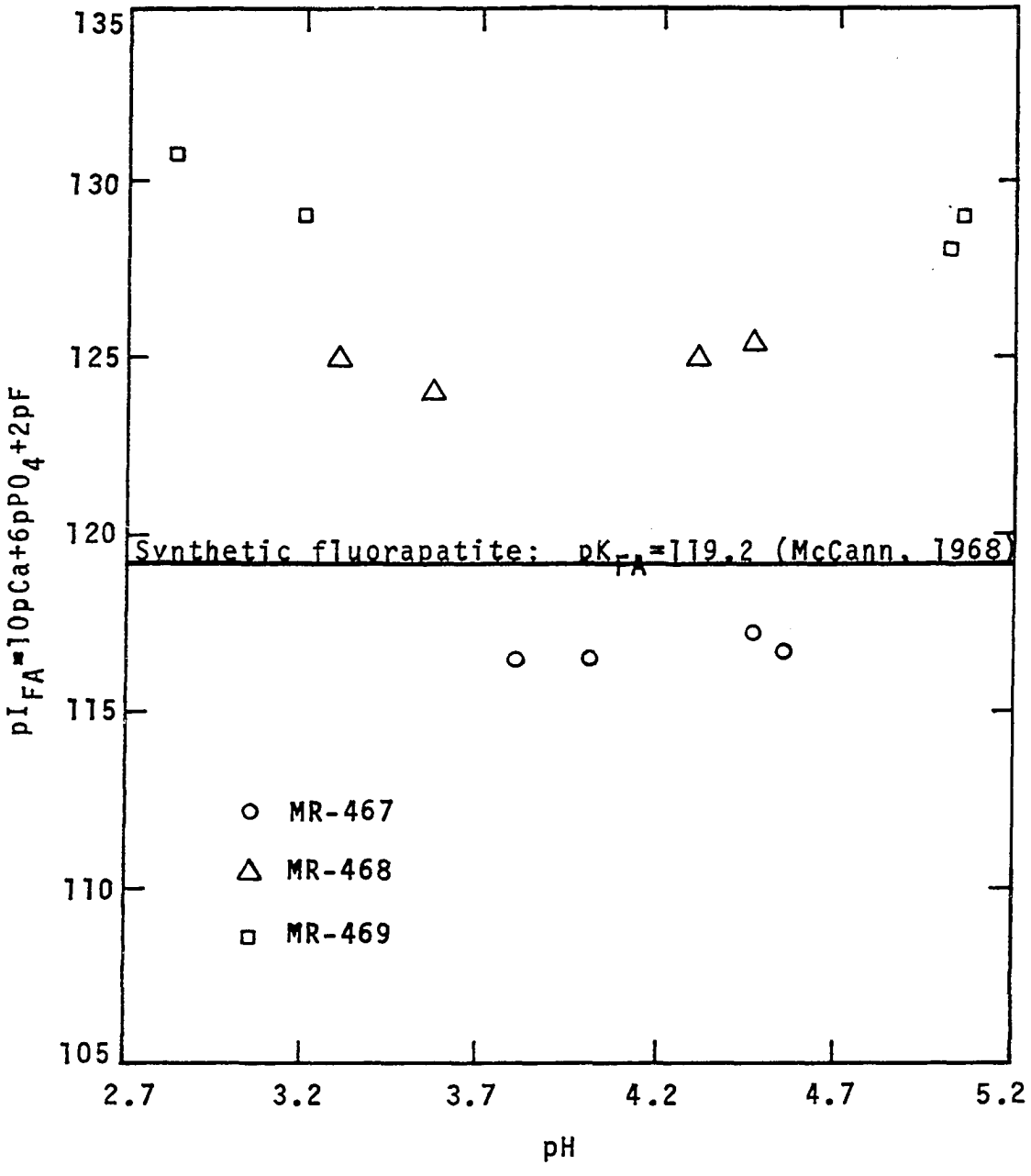

Figure 32. Plot of pI_{FA} versus pH of solutions equilibrated with three acid-extracted phosphate rocks at 25° C for 30 days

range. The solid-solution hypothesis would predict that the ion-activity products for fluorapatite for all the phosphate rocks would be located close together on the vertical scale and just above the horizontal line for synthetic fluorapatite, if the latter is the correct representation of the solubility-product constant for fluorapatite. If the ion-activity product obtained with sample MR-469 is the correct value for fluorapatite, the points for all the phosphate rocks should be close to the pI_{FA} values for MR-469 on the vertical scale.

The average values of pI_{CA} were calculated as 118.8, 125.5, and 129.4 for acid-extracted MR-467, MR-468, and MR-469 phosphate rocks, respectively. The acid-extracted phosphate rocks exhibited lower solubility than the citrate-extracted phosphate rocks. For citrate-extracted MR-467, MR-468, and MR-469 phosphate rocks, the average pI_{CA} values were 114.4, 118.7, and 121.2, respectively.

The calculated values of free energy of formation were -2949.8, -3046.8, and -3075.8 Kcal/mole for acid-extracted MR-467, MR-468, and MR-469 phosphate rocks, respectively. The free energy of formation for acid-extracted Florida phosphate was calculated as -2997.9 Kcal/mole based on the pK_{CA} value of 120.3 obtained in experiment 8. The values of free energy of formation for these acid-extracted phosphate rocks are plotted against the number of moles of carbonate per mole of apatite in Figure 33. The points for MR-505 phosphate rock and synthetic fluorapatite and the regression line for citrate-extracted phosphate rocks from Figure 31 are included for comparison. Again, the values for synthetic fluorapatite and phosphate rock sample MR-505 have been omitted from the calculations.

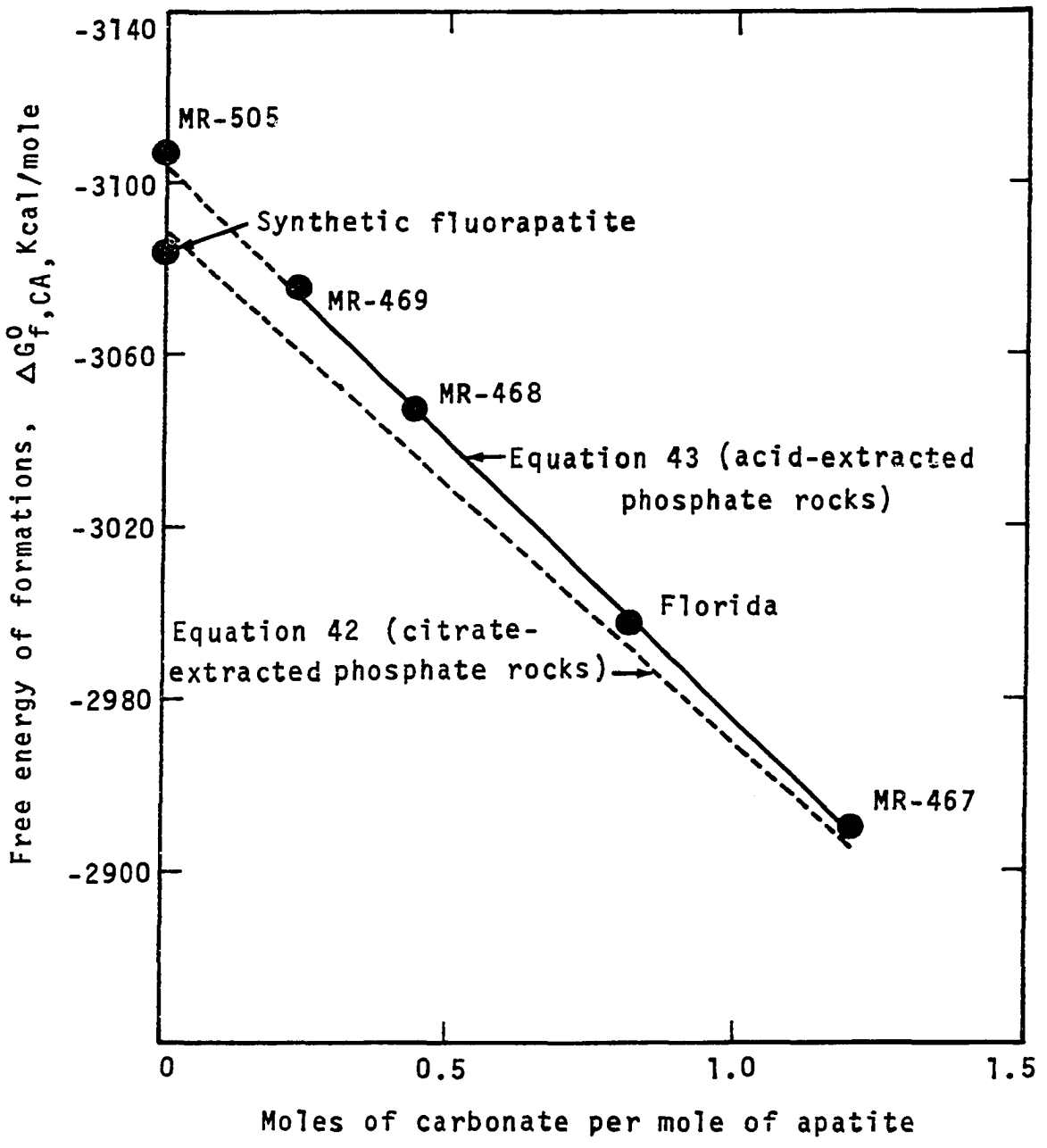

Figure 33. Plot of free energy of formation of apatites at 25° C versus number of moles of carbonate per mole of apatite in acid-extracted phosphate rocks. The value for MR-505 is for a citrate-extracted phosphate rock, and the value for synthetic fluorapatite is for unextracted material

The regression line in Figure 33 represents equation 43, developed from data on the acid-extracted phosphate rocks (MR-467, Florida, MR-468, and MR-469):

$$\Delta G^{o}_{f,CA} = -3104.9 + 130.3X \qquad (43)$$

where $\Delta G^{o}_{f,CA}$ is the free energy of formation of carbonate apatite and X is the number of moles of carbonate per mole of apatite.

The close fit of the points to a straight line in Figure 33 provides some verification that the ion-activity product for carbonate apatite is the proper one to calculate to represent the solubility. When analogous calculations were made on the basis of the ion-activity product of fluorapatite in solutions that had been equilibrated with the different phosphate rocks, the points did not fall as close to the line as did those shown in Figure 33.

One may note also that the regression line obtained with the acid-extracted samples in Figure 33 is above that obtained with the citrate-extracted samples, which signifies that the negative free energy of formation was greater and the solubility lower in the acid-extracted samples than in the citrate-extracted samples. Moreover, in the case of citrate-extracted phosphate rocks, the intercept at zero moles of carbonate per mole of apatite is close to the point for synthetic fluorapatite, and in the case of acid-extracted phosphate rocks the intercept is close to the point for a naturally occurring fluorapatite in an igneous phosphate rock. These observations agree with the findings made in previous experiments with the Florida phosphate rock and with the theory that the apatite within individual phosphate rocks exhibits differ-

ent activities and different solubilities. The observed difference in solubility between the synthetic fluorapatite and the naturally occurring fluorapatite may be accounted for on the basis of the better crystallinity of the latter.

SUMMARY

An investigation was made of the solubility of synthetic hydroxyapatite and some naturally occurring phosphate rocks in dilute HCl solutions. The equilibrium approach was used to determine whether the solubility behavior conforms to the solubility-product principle.

In the first experiment, a commercial hydroxyapatite was autoclaved with repeated additions of 1 N NH_4Cl solution to extract part of the solid. The solubility trials showed that the values obtained for the negative logarithm of the ion-activity product for hydroxyapatite (pI_{HA}) were similar with additions of 0.1 and 1 g of solid per 100 ml of solution, were similar (120.5 and 119.3), essentially independent of the pH, and higher than values obtained previously by other research workers. A plot of $-\log (a_{H^+}^3 \cdot a_{PO_4^{---}})$ against $-\log (a_{Ca^{++}} \cdot a^2_{OH^-})$ yielded a regression line with a slope of -1.69 which is close to the theoretical value of -1.67. This observation indicates that the solutions were in equilibrium with solid hydroxyapatite. The results are consistent with the theory that the hydroxyapatite in a given sample may have a range of activities, corresponding to a range of solubilities.

In the second experiment, a constant pH value (3.88) was obtained after 13 days of equilibration of 10-g quantities of Florida phosphate rock per 100 ml of dilute hydrochloric acid solution containing 3 meq. of HCl per 100 ml. The results of this preliminary study indicate that the 30-day period of contact used in subsequent experiments should be long enough for the solutions to become saturated with the apatite component in this phosphate rock.

In the third experiment, solutions equilibrated with Florida phosphate rock in the presence of fluorite were boiled, followed by equilibration for 5 days at 25° C. A plot of phosphate potential (pH_2PO_4 + ½pCa) against lime potential (pH - ½pCa) showed that the solutions were supersaturated with respect to fluorapatite plus fluorite at high pH - ½pCa values and unsaturated at low pH - ½pCa values. The suggestion was made that the unsaturation might result from inhibition of dissolution of the carbonate apatite as a consequence of formation of a layer of calcium fluoride on the surface at low pH values.

In the fourth experiment, addition of fluorite was found to have no effect on the solubility of Florida phosphate rock. Addition of 0.01 g of calcium carbonate to 1 g of Florida phosphate rock per 100 ml of solution caused the equilibrated solutions to be supersaturated with respect to both hydroxyapatite and fluorapatite plus fluorite at high pH - ½pCa values. From use of a fluoride-ion electrode in the fourth experiment, it was found that the activity of fluoride in solutions in contact with solid fluorite at low pH values could not be calculated from the solubility relation, pCa + 2pF = 9.84. The solutions were supersaturated with respect to fluorite at low pH values.

In the fifth experiment, analysis of the solutions indicated that they were saturated with fluorapatite and unsaturated with fluorite when suspensions of Florida phosphate rock were boiled and then equilibrated at 25° C for 10 hours. The negative logarithms of the ion-activity products for fluorapatite and fluorite were found to be 119.3 and 11.28, respectively, in comparison with values of 119.2 and 9.84 reported in the literature for the negative logarithms of the solubility-product

constants for the two compounds. When the equilibration period was extended to 67 days after boiling, the solutions were found to be supersaturated (pI_{FA} = 114.4) with respect to fluorapatite, and they were still unsaturated (pI_F = 11.57) with respect to fluorite.

In the sixth experiment, the ion-activity product for carbonate apatite in Florida phosphate rock was found as a function of ratio of solid to solution, pH of the solution after equilibration, and successive equilibrations. The negative logarithm of the ion-activity product, pI_{CA}, was found to be relatively constant within a certain range of pH. For the systems with 1 g of phosphate rock per 100 ml of solution, the values of the negative logarithm of the ion-activity product of carbonate apatite (pI_{CA}) were 116.3 and 117.9 for the first and second equilibrations, respectively. With 10 g of phosphate rock per 100 ml, the pI_{CA} values were the same (111.8) for the first and second equilibrations. These results may be explained by the theory that the carbonate apatite in Florida phosphate rock may have a range of activities, corresponding to a range of solubilities.

In the seventh experiment, an investigation was made of the solubility of citrate-extracted Florida phosphate rock. With 1 g of solid per 100 ml of solution, the pI_{CA} values were found to be 117.7 and 120.7 for the first and second equilibration, respectively. The calculated value of pI_{FA} was 119.7, which is close to the value of the negative logarithm of the solubility-product constant of synthetic fluorapatite (pK_{FA} = 119.2), for the second equilibration. The solutions thus appeared to be in equilibrium with both a carbonate apatite with very low surface activity and newly formed fluorapatite.

In the eighth experiment, pI_{CA} values of 116.6 and 110.8 were obtained in solubility measurements on systems in which 1- and 10-g quantities of Florida phosphate rock were equilibrated per 100 ml of solution. These two values are in good agreement with those obtained in the sixth experiment under similar conditions. Where the phosphate rock had first been extracted with 0.3 N HCl to remove different proportions of the solid, a relatively constant value of $pI_{CA} = 120.3$ was obtained regardless of the ratio of solid to solution and the degree of preliminary extraction. This figure is close to the value, $pI_{CA} = 120.7$, obtained in the second equilibration of citrate-extracted Florida phosphate rock with dilute solutions of hydrochloric acid in the seventh experiment. These findings suggest that the lowest value of the solubility-product constant for carbonate apatite in Florida phosphate rock may be in the range from $10^{-120.7}$ to $10^{-120.3}$. The average pI_{FA} value for the acid-extracted Florida phosphate rock was 119.2 regardless of the ratio of solid to solution and the degree of preliminary extraction. The value, 119.2, corresponds to the solubility-product constant of synthetic fluorapatite, which indicates that the solutions were in equilibrium with fluorapatite.

In the ninth experiment, the solubilities of several different phosphate rocks were investigated. These phosphate rocks covered a wide range of carbonate substitution in the apatite structure. Some of these phosphate rocks contained alkaline-earth carbonates, and indications were that, in the presence of sufficient alkaline-earth carbonate, there was no pH range in which a relatively constant value of pI_{CA} was obtained. When the phosphate rocks had been extracted with an alkaline ammonium citrate solution to eliminate the alkaline-earth carbonates prior to the

solubility measurements, however, a pH range in which the value of pI_{CA} was relatively constant was invariably present. The following values represent the averages of the negative logarithms of the ion-activity products for carbonate apatites in various citrate-extracted phosphate rocks in the pH range within which the values were relatively constant: MR-467, pI_{CA} = 114.4; MR-465, pI_{CA} = 118.7; MR-468, pI_{CA} = 118.7; MR-469, pI_{CA} = 121.2; and MR-505, pI_{FA} = 133.3. The pI_{CA} values increased with a decrease in number of moles of carbonate per mole of apatite. The ion-activity product for fluorapatite was much lower in citrate-extracted MR-505 phosphate rock (this rock was an igneous fluorapatite) than in synthetic fluorapatite (pK_{FA} = 119.2), perhaps because of the better crystallinity of the apatite in the rock.

A plot of the negative logarithm of the phosphorus concentration versus the pH of solutions that had been equilibrated with the various citrate-extracted phosphate rock showed that the phosphate rocks ranked in the following order of decreasing phosphorus concentration at a given pH value: MR-467 > MR-465, MR-468 > MR-469 > MR-505. The order of decreasing phosphorus concentration was the same as the order of decreasing substitution of carbonate for phosphate in the apatite present.

Free energies of formation, ΔG_f^o, for the various apatites were also calculated to investigate the activities of the apatites. The ΔG_f^o values for the apatites of the citrate-extracted phosphate rocks were as follows: MR-467, -2943.8 Kcal; Florida, -2994.3 Kcal; MR-465, -3035.6 Kcal; MR-468, -3037.6 Kcal; MR-469, -3064.6 Kcal; synthetic fluorapatite, -3087.3 Kcal; and MR-505, -3107.2 Kcal. A linear regression line was found when the ΔG_f^o values were plotted against the number of moles of carbonate per mole

of apatite for all the phosphate rocks except MR-505. The results conformed to the theoretical prediction that a linear relationship exists between the free energy of formation and the number of moles of carbonate per mole of apatite.

In the tenth experiment, the constant pI_{CA} values obtained were 118.8, 125.5, and 129.4 for acid-extracted MR-467, MR-468, and MR-469 phosphate rocks respectively. These values are all higher than those obtained with the citrate-extracted phosphate rocks. These results are in agreement with the theory that the carbonate apatites in the individual phosphate rocks had a range of activities, corresponding to a range of solubilities.

When the ΔG_f^o values were plotted against the number of moles of carbonate per mole of apatite, a linear regression line was found for the acid-extracted MR-467, MR-468, MR-469, and Florida phosphate rocks. The value for citrate-extracted MR-505 phosphate rock (the igneous fluorapatite) was very close to this new regression line. The new regression line, although located a little differently than the regression line obtained with the citrate-extracted samples, still conformed to the theoretical prediction that the free energy of formation of carbonate apatites should decrease as the degree of substitution of carbonate for phosphate decreases. The lower free energies of formation calculated for apatites in the acid-extracted phosphate rocks than in apatites in the citrate-extracted phosphate rocks are in accordance with the theory that the apatites in individual phosphate rocks have a range of activities, corresponding to a range of solubilities.

The results obtained in the tenth experiment indicated further that the apatites in the phosphate rocks investigated either (a) did not

conform to the solubility behavior expected if the carbonate apatites were a solid solution of carbonate apatite and fluorapatite or (b) conformed to the solid-solution concept but contained fluorapatites with widely differing solubilities. Because the ion-activity products for fluorapatite in the various phosphate rocks differed widely, the data do not support the view that the solutions were in equilibrium with solid fluorapatite having any particular solubility-product constant. The finding in the eighth experiment that the solutions in contact with Florida phosphate rock had an ion-activity product corresponding to the solubility-product constant of snythetic fluorapatite thus may have been a coincidence.

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APPENDICES

Appendix A

A Fortran Computer Program for Calculating the Unit-Cell Dimensions of Apatite in Phosphate Rock

The mathematical model for this computer program was described by McClellan and Lehr[1].

The original program, kindly supplied by Mr. J. R. Lehr, Tennessee Valley Authority, Muscle Shoals, Alabama, was designed for use on a G.E. 200 computer. The fortran program given here is a translation of the original program. The translated program was used in connection with an IBM 360 computer.

The experimental data needed for the program are the observed d-spacing values and their corresponding Miller indices (002, 300, 202, 310, 222, 312, 213, 321, 410, and 004). The first approximation of the lattice constants are those of unsubstituted fluorapatite, a = 9.3700 and c = 6.8800.

---

[1]McClellan, G. H., and Lehr, J. R. 1969. Crystal chemical investigation of natural apatites. American Mineralogist 54: 1374-1391.

```
      DIMENSION D(100),XH(100),XK(100),XL(100),XF1(100),PFA(100),W(100),
     1PFC(100),XR(100),XHKL(100),ISUB(100)
      K1=0

C1   ISETS IS THE NUMBER OF SAMPLES OF APATITE FOR WHICH THE UNIT-CELL
     ARE TO BE DETERMINED.

      READ(5,10) ISETS
   10 FORMAT(I6)
   20 K1=K1+1

C2   NP=NUMBER OF MILLER INDICES USED ( 10 IN THE PROGRAM AS USED IN THIS
     INVESTIGATION )
     A=9.3700 AND C=6.8800

      READ(5,30,END=300) NP,A,C
   30 FORMAT(I5,2F10.5)

C3   INSERT THE DATA OF D-SPACING VALUES WITH THEIR CORRESPONDING MILLER
     INDICES.

      READ(5,40) (D(I),XH(I),XK(I),XL(I),I=1,NP)
   40 FORMAT(F10.5,F6.3,2F6.1)
      DO 50 I=1,NP
      ISUB(I)=I
   50 W(I)=1./(D(I)**2)
      I2=0
      NP1=NP
   60 S00=0.
      S01=0.
      S11=0.
      S08=0.
      S18=0.
      S68=0.
      S78=0.
      S2=0.
      DO 70 I1=1,NP1
```

```
      I=ISUB(I1)
      XHKL(I)=(4./3.)*(XH(I)**2+XH(I)*XK(I)+XK(I)**2)+(A*XL(I)/C)**2
      XHKL(I)=SQRT(XHKL(I))
      XR(I)=(4.*((XH(I)**2)+(XH(I)*XK(I))+(XK(I)**2)))/(3.*A**2)+((XL(I)
     1**2)/C**2)
      XR(I)=SQRT(1.0000/XR(I))
      XF1(I)=D(I)-XR(I)
      S2=ABS(XF1(I))+S2
      PFA(I)=-((A*XL(I)/C)**2)/XHKL(I)+XHKL(I)
      PFA(I)=-PFA(I)/(XHKL(I)**2)
      PFC(I)=-(((A*XL(I)/C)**2)*A/C)/(XHKL(I)**3)
      S00=S00+W(I)*(PFA(I)**2)
      S01=S01+W(I)*PFA(I)*PFC(I)
      S11=S11+W(I)*(PFC(I)**2)
      S08=S08+W(I)*XF1(I)*PFA(I)
      S18=S18+W(I)*XF1(I)*PFC(I)
      S68=S68+W(I)*XF1(I)
   70 S78=S78+W(I)*(XF1(I)**2)
      B=S00*S11-(S01**2)
      DA=(S11*S08-S01*S18)/B
      DC=(S00*S18-S01*S08)/B
      A=A-DA
      C=C-DC
      IF(NP1-2) 270, 270, 100
  100 S1=ABS((S78-(DA*S08)-(DC*S18))/(NP1-2.))
      S=SQRT(S1)
      S2=SQRT((S2)/(NP1-2))
      SEA1=ABS(S11/B)
      SEA=S*SQRT(SEA1)
      SEC1=ABS(S00/B)
      SEC=S*SQRT(SEC1)
      SF2=S68**2/NP1
      R1=ABS((DA*S08+(DC*S18)-SF2)/(S78-SF2))
      R=SQRT(R1)
      WRITE(6,110) A,SEA,C,SEC,S,R,DA,DC
  110 FORMAT('0', 2F20.5)
      WRITE(6,120)
```

```
120 FORMAT(//  9X,'DOBS',11X,'DCALC',10X,'DIFF',8X,'H',7X,'K',7X,'L')
    DO 130 I1=1,NP1
    I=ISUB(I1)
130 WRITE(6,140) D(I),XR(I),XF1(I),XH(I),XK(I),XL(I)
140 FORMAT(3F15.5, 3F8.1)
    I2=I2+1
    IF(20-I2) 280, 280, 150
150 DA=ABS(DA)
    DC=ABS(DC)
    IF(DA-.00001) 160, 160, 60
160 IF(DC-.00001) 170, 170, 60
170 WRITE(6,180) A,SEA,C,SEC,R,S,S2
180 FORMAT(// 7X,'A AND STANDARD ERROR IN A ARE ', 2F20.5// 7X,
   1'C AND STANDARD ERROR IN C ARE ', 2F20.5// 7X,'R AND STANDARD ERRO
   1R IN D ARE ',2F20.5// 7X,'SQUARE ROOT OF SUM DELTA D DIVIDED BY NP
   1-2= ', F20.6)
    ISB=0
    DO 250 I1=1,NP1
    I=ISUB(I1)
    SS=1.
    IF(S*SS-ABS(XF1(I))) 220, 240, 240
220 WRITE(6,230) XH(I),XK(I),XL(I),XF1(I)
230 FORMAT(// 7X,'ERROR IN ', 3F8.1// 7X,'XF1= ', F15.5)
    GO TO 250
240 ISB=ISB+1
    ISUB(ISB)=ISUB(I1)
250 CONTINUE
    IF(ISB-NP1) 260, 270, 270
260 NP1=ISB
    GO TO 60
270 IF(K1-ISETS) 20, 300, 300
280 WRITE(6,290)
290 FORMAT(// 7X,'** ITERATION NOT WORKING **')
    GO TO 270
300 STOP
    END
```

Appendix B

A Fortran Computer Program for Calculating the Activities of Calcium and Phosphate Ions in Solutions Equilibrated with Apatites

The experimental data needed for the program are pH, calcium concentration (moles per liter), and total inorganic phosphorus concentration (moles per liter). The three dissociation constants of orthophosphoric acid are $K_1 = 7.586 \times 10^{-3}$, $K_2 = 6.31 \times 10^{-8}$, and $K_3 = 4.79 \times 10^{-13}$. The dissociation constants of ion-pairs are 8.4×10^{-2} and 2.0×10^{-3} for $(CaH_2PO_4)^+$ and $(CaHPO_4)^0$, respectively.

The ionic strength of the solution is estimated by assuming it is equal to three times the calcium concentration plus three times the concentration of mercury added as mercuric chloride (0.001M in this investigation).

```
      DIMENSION LOC(22),PH(12,12),CA(12,12),PT(12,12),B(12,12),A(12,12),
     1TPCA(12,12),P2OH(12,12),PP(12,12),SIXP(12,12),PH2P(12,12),
     1SUM(12,12),FINAL(12,12),PCA(12,12),PCCA(12,12),PPT(12,12),
     1POH(12,12),PP3(12,12),PHP(12,12),PFA(12,12),PCDA(12,12),
     1PACC(12,12),PCDC(12,12),PCMA(12,12),CDC(12,12),CMC(12,12)

C1   M IS THE NUMBER OF SETS OF DATA TO BE CALCULATED. THE MAXIUM VALUE OF
     M IS 12 PER CYCLE IN THE COMPUTATIONS. TO STOP THE PROGRAM, INSERT
     A CARD WITH M=0.

     5 READ(5,1)M,(LOC(I),I=1,12)
       IF(M)99,99,4
     1 FORMAT(I3,21A3)

C2   THREE DATA CARDS (PH, CALCIUM CONCENTRATION, AND TOTAL PHOSPHORUS
     CONCENTRATION) ARE NEEDED PER CYCLE IN THE COMPUTATIONS.

     4 READ(5,2)(PH(I,1),I=1,M)
       READ(5,3)(CA(I,1),I=1,M)
       READ(5,3)(PT(I,1),I=1,M)
     2 FORMAT(20F4.2)
     3 FORMAT(8E10.3)
       DO 12 I=1,M

C3   PCCA=NEGATIVE LOGARITHM OF CALCIUM CONCENTRATION.
     PPT=NEGATIVE LOGARITHM OF TOTAL PHOSPHORUS CONCENTRATION.

       PCCA(I,1)=-ALOG10(CA(I,1))
       PPT(I,1)=-ALOG10(PT(I,1))

C4   PH+POH=14.0

       P2OH(I,1)=(28.-(2.*PH(I,1)))
       POH(I,1)=P2OH(I,1)/2.0
       AA=-PH(I,1)
       BB=2.*AA
       CC=3.*AA
```

```
C5  THE TENTH APPROXIMATIONS OF THE ACTIVITIES OF CALCIUM AND ORTHOPHOSPHATE
    IONS ARE USED TO CORRECT THE ACTIVITIES OF CALCIUM AND ORTHOPHOSPHATE
    IONS, AS CALCULATED FROM THE DEBYE-HUCKEL EQUATION, FOR THE FORMATION
    OF ION-PAIRS.

      N=10
      DO 20 J=1,N
      B(I,J)=(ALOG10(CA(I,J))*10.)

C6  THE IONIC STRENGTH OF THE SOLUTION IS ESTIMATED BY ASSUMING IT IS
    EQUAL TO THREE TIMES THE CALCIUM ION CONCENTRATION PLUS THREE TIMES
    THE CONCENTRATION OF MECURY ADDED AS MECURIC CHLORIDE (0.001 M).

      A(I,J)=SQRT(CA(I,J)*3.+0.003)

C7  DEBYE-HUCKEL EQUATION
                  LOG R = -(0.5092*Z**2.0*I**0.5)/(1.0+B*I**0.5)
    WHERE R IS THE ION ACTIVITY COEFFICIENT, Z IS THE ION ELECTRIC
    CHARGE, I IS THE IONIC STRENGTH OF THE SOLUTION, AND B IS A CONSTANT.
    LET A(I,J)=I**0.5
    NOW -LOG(10*CA ACTIVITY)=-LOG(10*R)-LOG(10*CA CONCENTRATION)
    AND -LOG(10*R)=(0.5092*2**2*10*A(I,J))/(1.0+1.972*A(I,J))
    WHERE 1.972 IS THE VALUE OF B IN THE DEBYE-HUCKEL EQUATION.

      TPCA(I,J)=((A(I,J)*20.37)/(1.+(1.972*A(I,J))))-B(I,J)

C8  PCA=NEGATIVE LOGARITHM OF CA ACTIVITY

      PCA(I,J)=TPCA(I,J)/10.0

C9  PP=PH-1/2 PCA

      PP(I,J)=PH(I,1)-(TPCA(I,J)/20.)

C10 WE WANT TO CALCULATE THE ACTIVITY OF PO4 ION FROM THE FOLLOWING RELATION
      PT/PO4=((H**3)/(K1K2K3))+((H**2)/(K2K3*R OF H2PO4))+((H)/(K3*
```

```
          R OF HPO4))+(1/(R OF PO4))
    WHERE K1,K2 AND K3 ARE THREE DISSOCIATION CONSTANTS OF ORTHOPHOSPHORIC
    ACID, AND H IS HYDROGEN ION ACTIVITY.
    DENOM=(1.0+1.397*A(I,J))*(1.0+1.314*A(I,J))
    WHERE 1.397 IS THE B VALUE FOR H2PO4 AND 1.314 IS THE B VALUE FOR BOTH
    HPO4 AND PO4 IN THE DEBYE-HUCKEL EQUATION.

      DENOM=1.+2.710*A(I,J)+1.834*(A(I,J)*A(I,J))

C11 BETA=-(0.5092*A(I,J))/(1.0+1.397*A(I,J))-(0.5092*2**2*A(I,J))/(1.0+

      BETA=((-7.129*A(I,J))-(9.910*(A(I,J)*A(I,J))))/DENOM

C12 DELTA=-(0.5092*2**2*A(I,J))/(1.0+1.314*A(I,J))-(0.5092*3**2*A(I,J))/
        (1.0+1.314*A(I,J))

      DELTA=(-6.620*A(I,J))/(1+1.314*A(I,J))

        (1.0+1.314*A(I,J))

C13 GAMMA=-(0.5092*A(I,J))/(1.0+0.391*A(I,J))-(0.5092*3**2*A(I,J))/
      GAMMA=((-5.092*A(I,J))-(7.067*(A(I,J)*A(I,J))))/DENOM

C14 ALPHA=-(0.5092*A(I,J))/(1.0+1.397*A(I,J))-(0.5092*2**2*A(I,J))/
        (1.0+1.314*A(I,J))

      ALPHA=(-2.546*A(I,J)-(3.513*(A(I,J)*A(I,J))))/DENOM

C15 TOP=PT(I,J)*K1K2K3*R OF H2PO4*R OF HPO4*R OF PO4
    WHERE K1=7.586E-3, K2=6.31E-8, AND K3=4.79E-13

      TOP=(PT(I,J)*2.291E-22)*10**BETA

C16 BOT=(H**3*R OF H2PO4*R OF HPO4*R OF PO4)+(H**2*K1*R OF HPO4*R OF
        PO4)+(H*K1K2*R OF H2PO4*R OF PO4)+(K1K2K3*R OF H2PO4*R OF HPO4)

      BOT=10**CC*10**BETA+7.586E-3*10**BB*10**DELTA+
```

```
     14.787E-10*10**(AA+GAMMA)+2.291E-22*10**ALPHA

C17 QUO=ACTIVITY OF PO4 ION

       QUO=TOP/BOT

C18 TO OBTAIN THE POSITIVE VALUE OF PPO4

       CN=0.0
    14 CN=CN+1.0
       QUO=QUO*10.
       IF(QUO-1.)14,14,15
    15 QUOL=ALOG10(QUO)-CN
       SIXP(I,J)=-6.*QUOL
       PP3(I,J)=-QUOL

C19 PK2+PK3=7.20+12.32=19.52

       PH2P(I,J)=-BB-19.52-QUOL
       PHP(I,J)=PH2P(I,J)+7.20-PH(I,1)

C20 DISSOCIATION CONSTANT,D1,OF ION-PAIR(CAH2PO4) IS 8.4E-2 OR PD1=1.076.

       PCDA(I,J)=PCA(I,J)+PH2P(I,J)-1.076
       PACC(I,J)=((0.5092*A(I,J))/(1.+(1.9716*A(I,J))))

C21 CDC=CONCENTRATION OF ION-PAIR (CAH2PO4)

       PCDC(I,J)=PCDA(I,J)-PACC(I,J)
       CDC(I,J)=10**(-PCDC(I,J))

C22 DISSOCIATION CONSTANT ,D2, OF ION-PAIR(CAHPO4) IS 2.0E-3 OR PD2=2.699.

       PCMA(I,J)=PCA(I,J)+PHP(I,J)-2.699

C23 CMC=CONCENTRATION OF ION-PAIR (CAHPO4)
```

```
      CMC(I,J)=10**(-PCMA(I,J))

C24 CA(I,J+1)=CORRECTED CALCIUM ION CONCENTRATION FOR TWO ION-PAIRS

   19 CA(I,J+1)=ABS(CA(I,1)-CDC(I,J)-CMC(I,J))

C25 PT(I,J+1)=CORRECTED TOTAL PHOSPHORUS CONCENTRATION FOR TWO ION-PAIRS

   20 PT(I,J+1)=ABS(PT(I,1)-CDC(I,J)-CMC(I,J))
   21 PFA(I,N)=9.0*PCA(I,N)+SIXP(I,N)
      SUM(I,N)=TPCA(I,N)+P2OH(I,1)+SIXP(I,N)
   12 FINAL(I,N)=PH2P(I,N)+(TPCA(I,N)/20.0)
      WRITE(6,51)(LOC(I),I=1,12)
   51 FORMAT(1H1,52HCALCULATING SOLUBILITIES     S.H. CHIEN   EXPERIMENT
     1,21A3,//)
      WRITE(6,52)
   52 FORMAT('0',T3,'SA',3X,'PH',4X,'PCCA',3X,'PPT',4X,'PCA',
     15X,'PH2PO4',2X,'PHPO4',3X,'PPO4',4X,'POH',2X,'10PCA+2POH+6PPO4',
     12X,'PH-(PCA)/2',2X,'PH2PO4+(PCA)/2',2X,'9PCA+6PPO4')
      DO 54 I=1,M
   54 WRITE(6,55)I,PH(I,1),PCCA(I,1),PPT(I,1),PCA(I,N),PH2P(I,N),
     1PHP(I,N),PP3(I,N),POH(I,1),SUM(I,N),PP(I,N),FINAL(I,N),PFA(I,N)
   55 FORMAT('0',T3,I2,4F7.3,4F8.3,3X,F9.3,6X,F8.3,6X,F8.3,7X,F8.3)

C26 REPEAT ANOTHER CYCLE OF COMPUTATION WITH M SETS OF DATA.

      GO TO 5
   99 STOP
      END
```

Appendix C. Significance of Alkaline-Earth Carbonates in Solubility Relations of Apatites

Introduction

In experiment 4, the ion-activity product for carbonate apatite in Florida phosphate rock was found to be greater in the presence of calcium carbonate than in its absence. In experiment 9, similar results were obtained with other phosphate rocks containing alkaline-earth carbonates. Indications are that, when sufficient alkaline-earth carbonate is present, there is no pH range in which the ion-activity product for carbonate apatite is relatively constant. The objective of the experiment reported in this Appendix was to obtain information on the mechanism of the alkaline-earth-carbonate effect.

Procedure

Two 10-g samples of Florida phosphate rock that had previously been extracted with alkaline ammonium citrate were used. A 0.04-g quantity of <100-mesh dolomite was added to one of the samples. The samples were then equilibrated at 25° C with 100-ml volumes of solution containing 3 meq. of HCl. The pH of the suspensions was determined at intervals up to 77 days.

Results and discussion

Table 25 gives the results of the pH measurements. At all times, the pH value of the suspension containing dolomite was higher than that of the suspension without dolomite. Moreover, the time required for the pH to rise to a stable value was greater in the presence of dolomite than

in its absence (58 days versus 13 days). The second observation indicates that dolomite may continue to affect the pH of the solution after dissolution of the carbonate apatite has ceased.

Table 25. pH of solutions after different times of equilibration of citrate-extracted Florida phosphate rock with dilute HCl in the presence and absence of dolomite at 25° C

Time in days	pH		Time in days	pH	
	Phosphate rock	Phosphate rock plus dolomite		Phosphate rock	Phosphate rock plus dolomite
1	3.52	4.14	23	3.68	6.80
3	3.62	4.83	30	3.70	6.87
6	3.63	5.46	41	3.70	6.92
9	3.65	5.80	58	3.70	7.00
13	3.70	6.25	70	3.72	7.02
17	3.67	6.54	77	3.70	7.00

The significance of the pH effect of alkaline-earth carbonates just described may be inferred with the aid of observations made by other investigators. Chaverri (1962) found that the concentrations of calcium and phosphorus in dilute HCl solutions equilibrated with Florida phosphate rock remained substantially constant from the first day onward, but the pH value increased appreciably over a long time. The solution was finally supersaturated with respect to both hydroxyapatite and fluorapatite plus fluorite. Wier (1968) found that solutions once supersaturated with respect to apatite may remain supersaturated indefinitely at room temperature.

The implication of these findings in terms of the mechanism of the

alkaline-earth-carbonate effect is seen as follows: The dilute HCl solutions used for equilibration initially have relatively low pH values. The pH rises due to interaction of the acid with the apatite. If no foreign substances are present, an equilibrium condition is soon reached in which the solution is saturated with the apatite. Further reaction of the acid with the solid then ceases, and the condition of saturation persists indefinitely. When the apatite is associated with foreign substances such as alkaline-earth carbonates that react slowly with acid, saturation of the solution with apatite no longer controls the equilibrium pH value. The pH rises above the equilibrium value. Because the apatite constituents that were dissolved under the more acid conditions remain in solution and do not reprecipitate at room temperature when the pH has risen above the equilibrium value, a condition of supersaturation results. The ion-activity products obtained under these conditions thus serve merely to indicate the degree of supersaturation.